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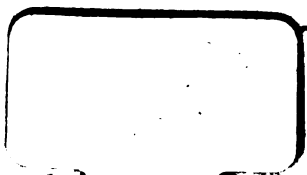
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**AMEDEO AVOGADRO (1776-1856)**

**Professor in the University of Turin, Italy. Renowned for formulating the fundamental principle of modern chemistry known as Avogadro's Hypothesis.**  
**From a photograph of a statue erected to his memory**

# A COURSE IN GENERAL CHEMISTRY

BY

WILLIAM McPHERSON

AND

WILLIAM EDWARDS HENDERSON

PROFESSORS OF CHEMISTRY, OHIO STATE UNIVERSITY

*SECOND EDITION*



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## PREFACE

In preparing this textbook in general chemistry the authors have been guided by a few simple principles. They have endeavored to write a book scientific in spirit and at the same time thoroughly teachable. It may be said at once that the text presents few novelties, either in arrangement or in method. While individual teachers can succeed better by adopting unusual and original modes of presentation, we appear to have reached a more or less standard method, which is, on the whole, best adapted to the greatest number.

The most noticeable departure from this arrangement in the present text is the postponement of the halogen elements to a relatively late chapter. Several considerations of pedagogy have prompted this change: (1) The student needs some training in experimental manipulation before attempting laboratory exercises with these active elements. (2) The action of these elements upon the alkalies, and the conduct of their oxygen acids, involve many difficulties, and the attempt to meet these by presenting the chemistry of these elements in several widely separated chapters is bewildering to the student. (3) It is unsatisfactory to develop the conception of an acid by means of the example of the halogen hydrides, since they are far from being typical acids. In the experience of the authors the order followed in this text is much to be preferred.

In the main the elements have been grouped in description in accordance with their positions in the periodic classification, but the authors have not hesitated to abandon this order when a more natural one suggested itself. Thus, with the metals the arrangement chosen presents the strongly electropositive elements of unchanging valence first. These are followed by those

which present the complications of changeable valence, sulfide metallurgy, and amphoteric characteristics.

Every teacher desires to impress his students with the truth that science rests fundamentally upon experiment and is therefore subject to the uncertainties of experimental error. The authors believe that this end is best attained by the free introduction of historical matter. This gives to abstractions a personal touch which makes them seem human — more a product of experience and imagination and less of the nature of a revelation. While the adoption of this method has added materially to the size of the book, it is believed that it has increased its interest and at the same time kept it faithful to the spirit of science.●

The treatment of theory in any text will always leave many teachers dissatisfied. Each has his own point of view, and the authors have simply been loyal to their own. They have had no partisan feeling for any particular theory, but, on the contrary, have consistently tried to impress the student with the idea that theories are largely a matter of convenience and are not to be regarded as final.

A rather unusual amount of material has been introduced which might fairly be left to the course in physics. With the elective system so widely adopted in American colleges it can no longer be assumed that a student has had a course in physics before entering upon the study of chemistry. Moreover, it is a rather common experience to find that the knowledge which a student has acquired in one course is with some difficulty called to his assistance in another.

The extent to which the elements of organic chemistry should be incorporated into the general course must always be decided by local conditions. The present text includes a chapter on the compounds of carbon, which the authors feel is in good proportion to the other chapters. Most of this may be omitted if the requirements of a course render this desirable.

In the matter of spelling the various chemical terms, the authors have been conservatively modern. The shorter method

for spelling *sulfur* is now so generally used that there seems to be no good reason opposed to its universal adoption.

The growing importance in the industries of some of the rarer metals renders a more intimate knowledge of their properties desirable. Accordingly, the discussion of these metals is somewhat more extended than is usual in a text of this scope.

The authors have frankly adopted all the devices of paragraphing and typography which would make the logical argument and the coördination of matter stand out prominently. They have also endeavored to have the drawings true to scale and representing ordinary laboratory apparatus. They were made by Mr. Cree Sheets under the direction of our colleague, Professor Thomas E. French, of the department of engineering drawing.

No effort has been spared to have the statements concerning industrial processes accord with present usage, and we are indebted to our colleague, Professor James R. Withrow, as well as to the managers of many industrial concerns, for much information along these lines. Other colleagues have given us the benefit of expert knowledge in special topics, among whom we desire to name Professor Edward Orton, Jr., department of ceramics; Professor Edward E. Somermeier and Professor Dana J. Demorest, department of metallurgy; and Professor Charles B. Morrey, department of bacteriology. Finally, we owe much to the experience and kindly interest of the associates in our own department, Professors Charles W. Foulk and William L. Evans, and Dr. David R. Kellogg, who has corrected all the proof sheets. To all those whom we have mentioned, and to many other friends as well, we here express our deep sense of gratitude. At the same time we wish to emphasize the fact that the authors alone are responsible for any errors which may be found in the text.

THE AUTHORS

THE OHIO STATE UNIVERSITY



## PREFACE TO THE SECOND EDITION

The years that have elapsed since the publication of this text have rendered a revision desirable. The book has been largely rewritten, and a number of changes have been made in the order of arrangement looking toward simplicity of presentation. Some of these changes are not in accord with the views expressed in the preface of the First Edition. The years of experience with the First Edition, however, have convinced the authors that the order of presentation now adopted is the preferable one, and this view is also shared by many other teachers whose judgment the authors value. Much of the illustrative material has been put into minor type, not to minimize its importance but to indicate that it is not essential to an understanding of subsequent pages. To some extent certain theoretical portions have been accorded the same typographical treatment. The chemical developments incidental to the World War have been of such great importance, not only because of actual achievements but as showing the wonderful potential possibilities in chemistry for meeting economic demands, that the authors have freely incorporated items of war triumphs in the hope of inspiring the student with the forward look and the possibilities of the future days in Chemistry.

The authors desire to express their appreciation to the many teachers who, from time to time, have made valuable suggestions and especially to their colleague, William J. McCaughey, Professor of Mineralogy, and to Mr. Cloyd D. Looker, who has assisted in reading the proof.

THE AUTHORS

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# **A COURSE IN GENERAL CHEMISTRY**



# GENERAL CHEMISTRY

## CHAPTER I

### MATTER AND ENERGY

**Introduction.** We early learn in common experience that all material things with which we are acquainted are constantly undergoing changes of some sort. Each succeeding season profoundly alters the whole aspect of nature around us. Even those things which we consider to be the most durable, in time show evidences of change. The metals rust away; the solid rocks weather and disintegrate; the most imposing buildings crumble into ruins. The variety of such changes in nature is almost without limit, yet it is possible to resolve them all into two fundamental factors, — the *matter* which undergoes change, and the *energy* which occasions the change or results from it.

Many of these changes result in the formation of substances which are at once recognized to be different from the original materials. When iron rusts, it is evident that the rust is quite different from the iron. When a lump of coal burns, the invisible gases and handful of ashes into which it is converted bear no resemblance to the coal. These examples suggest many questions as to the real nature of these changes, — why they occur, and in what respects the products differ from the original materials.

**The science of chemistry.** The science of chemistry has for its object the accurate investigation of all such changes as have just been described, the causes which occasion them, the energy changes which accompany them, and the laws in accordance with which they take place. Chemistry is therefore very intimately concerned with both matter and energy, and it will be of much advantage if at the outset we get clearly before us some fundamental conceptions in regard to these two things.

## MATTER

We think of matter as being anything that has mass or weight, and this is by far the most fundamental characteristic of matter.

**Mass.** If a given force is applied to a body, the body will gain a certain acceleration, and experience shows that, in general, the same force applied to two different bodies will give them different accelerations. For example, the same force applied successively to a cube of lead and to a similar cube of wood will give a much greater acceleration to the wood than to the lead. *The property of a body that determines the acceleration it will acquire when acted upon by a given force is called its mass.*

**Weight.** The force in nature with which we are most familiar is gravity, and we usually get our impression as to the quantity of matter constituting a body from our muscular sensations in opposing the force of gravity,—in other words, by lifting the body. A spring balance records the same quantity in a mechanical way, the scale on such a balance being made by marking the points to which a series of arbitrary units stretch the spring. What is really measured in this way is the intensity of the earth's attraction for the body or the acceleration it tends to impart to the body. Since this varies with the distance of the body from the center of the earth, it is evident that the same body will not have the same weight at places of different elevation. *The measure of the earth's attraction for a body is called its weight.*

**Weight proportional to mass.** If the force of gravity were constant at all points on the earth, we could make use of this force to measure mass directly, and would not need to make a distinction between mass and weight; but this is not the fact. However, if two bodies have the same weight in one locality, they will have equal weights in all other localities; for if the force of gravity has changed, the change will affect both bodies equally. Consequently the weights of two bodies are always *proportional* to their masses, and it is only occasionally that we need to keep in mind the distinction between the two terms.

**Unit of mass.** The unit of mass which is universally employed in scientific work is the *gram*. This is the one thousandth part

of the mass of a particular piece of platinum preserved in the International Bureau of Weights and Measures at Sèvres near Paris, and called the standard kilogram. This piece of platinum was originally so chosen that the mass of a gram would exactly equal that of one cubic centimeter of water at 4° centigrade. Unfortunately the effort to have this so was not entirely successful, and one cubic centimeter of water does not have a mass of precisely one gram, though the difference is very slight.

**Conservation of mass.** Since the outward form and condition of matter are constantly changing, it would perhaps seem reasonable to suppose that its mass is also undergoing variation. The mass of a lump of coal is certainly much greater than that of the ashes which result from its burning. However, if we collect the gases formed and take into account all the materials concerned in the burning, we find that the total mass remains unchanged. All our experience goes to show that this is true in every change in matter, and that *mass can neither be created nor destroyed*.

**Density.** The density of a body is the mass of its unit volume, that is, of one cubic centimeter. Since this volume of water has a mass of almost exactly one gram, the figures which state the density of a body at the same time tell how many times as heavy as water it is. Thus lead has a density of 11.37, which means that 1 cc. weighs 11.37 g., and also that, volume for volume, lead is 11.37 times as heavy as water.

Gases are so very light that their densities must be expressed in numbers which are inconveniently small, that of oxygen being 0.001429. Such numbers are called the *absolute* densities, to distinguish them from the *relative* densities, or *specific gravities*, which are more often employed. The relative density is the ratio between the mass of a given volume of one gas to that of some other gas chosen as a standard. For many years air was employed as the standard gas, so that a statement of the relative density of a gas was equivalent to a statement of how many times as heavy as air it is. It is coming to be the custom to compare gases with

oxygen and to assign the latter a value of 16 instead of unity, in order that the density of hydrogen, the lightest of gases, may not be less than unity. On this basis, the statement that the density of nitrogen is 14.01 means that, volume for volume, the mass of nitrogen is to that of oxygen as 14.01 is to 16. In describing a gas it is more usual to state the weight of one liter than to give its density. A table giving such weights for a number of gases will be found in Appendix B.

**The properties of substances.** By the term *properties* is meant all of those marks or characteristics by which a given substance is identified. Many of these properties are designated by words in common use, such as *color*, *hardness*, *luster*, *transparency*, *solubility*, *melting point*, *boiling point*, and *physical state* (that is, whether solid, liquid, or gas). Others are not so obvious to an untrained observer, among these being *density*, *refractive index*, *conductivity* for heat and electricity, and *crystalline form*.

All of these properties are the peculiar marks of the substance itself, and are the means by which we identify the substance. They are, however, greatly modified by the physical conditions under which they are observed, such as the temperature and the pressure. Thus red oxide of mercury becomes nearly black when heated, but recovers its original color when cooled. Water decreases in density with rise of temperature, as do nearly all liquids, so that the warmer water tends to rise to the top. All gases may be converted into liquids by pressure at low temperatures, and the boiling point of a liquid, as well as its freezing point, depends upon the pressure.

## ENERGY

Since every change in matter involves a change in energy, we must consider some of the characteristics of energy before going on to a more careful study of the variety of changes in matter.

**Definition of energy.** In everyday language we sometimes say that a certain man is full of energy, meaning that he has a great capacity for work. We also recognize the same quality in

inanimate things. We realize that steam, highly compressed in a boiler, possesses energy, for we know that when it is admitted to the cylinder of the locomotive it will push back the piston and move the train. Energy is present in electric power lines, for a motor connected with them is caused to rotate, an electric lamp to give light, a resistance heater to supply heat. Energy must be expended in raising a block of stone to the top of a building, and when there it too possesses energy, for by its fall it will produce effects which we recognize to be due to the expenditure of energy. *We may therefore define energy as the ability to do work.*

**Varieties of energy.** Energy appears in many forms, among the most familiar of which are heat energy, electrical energy, and kinetic energy, or the energy of moving bodies. No less important is the potential energy which a body possesses by virtue of its position. This represents the work done upon a body in raising it to a height, and which can then be recovered in other forms when the body falls.

**Conservation of energy.** The experience gained in a century of experimenting has convinced scientists that, like mass, *energy can be neither created nor destroyed*, and this generalization is known as the *law of conservation of energy*. It is not difficult, however, to alter the distribution of energy between bodies. If a piece of hot metal is dipped into water, the metal is cooled and the water is heated, so that the metal loses energy and the water gains it. When a swinging bat strikes the ball, the latter gains energy while the bat loses it. There is therefore no constant quantity of energy in a given body as there is mass.

**Transformation of energy.** Moreover, energy can be freely transformed from one variety into another. The heat energy of burning coal can be changed into the kinetic energy of the locomotive. The kinetic energy of falling water can be transformed into electrical energy, as in the power plants of Niagara Falls. The electrical energy of the trolley line is readily converted into the kinetic energy of the moving car. In all such

transformations a *definite quantity of energy of one kind always gives a definite quantity of another*. We can therefore speak of the mechanical equivalent of heat, meaning the quantity of mechanical or kinetic energy that can be obtained from a given quantity of heat energy. In a similar way we speak of the electrical equivalent of mechanical energy or the heat equivalent of electrical energy.

**Illustration of transformation of energy.** The diagram (Fig. 1) illustrates a few familiar transformations of energy. The heat of the flame *A* is converted into mechanical energy in the heat engine *B*. The motion of

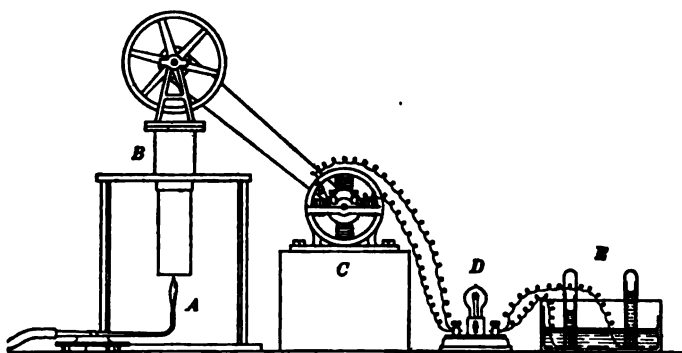


FIG. 1

the engine is communicated to the small dynamo *C*, where it is converted into magnetic and electrical energy. The electrical energy is changed into heat and light in the incandescent lamp *D*, and into chemical energy (see following paragraph) in the electrical decomposition of a solution in the cell *E*.

**Chemical energy.** Among the most important kinds of energy is that form which is called chemical energy. In the next chapter it will be shown that when a substance burns in the air, the change occurring is due to the action upon it of an invisible gas called oxygen. When a strip of magnesium ribbon is burned, it is converted into a white ash and a great deal of heat is given off, together with an intense light. Since we accept the law of conservation of energy as true, we argue that this heat

must have come from some other form of energy present in the magnesium and oxygen. This conclusion is strengthened when we find by experiment that in order to recover the magnesium and the oxygen from the white ash, work must be done equivalent to the heat set free when the magnesium burned. The latter can then burn once more with the same evolution of heat as in the former experiment.

The case is similar in many respects to the more familiar one presented by falling bodies. When a body falls from a height and strikes the earth, its potential energy is turned into mechanical effects and heat. To restore the body to the height, work must be done upon it equivalent to the energy set free in its fall. This work is in some way stored within the body as energy, for it may once more fall with the same effects as before. We do not know how the energy is stored within the body, but we do know that it is, and we name it potential energy. We say that the *cause* of the fall of the body is the attraction of gravity. Under the influence of this force a body falls toward the earth and its potential energy changes into kinetic energy. We can measure the force of gravity, and we know the laws regulating the fall of bodies, but we do not understand the nature of gravity nor how it acts.

In a similar way we give the name *chemical energy* to that form of energy which becomes apparent when substances combine with each other, and we say that they combine because of the force of *chemical attraction* or *affinity*; but we do not know anything more about the nature of chemical energy than we do about potential energy, nor do we know anything more about the force of chemical affinity than we know about the force of gravity. These terms are merely names for things which we know to exist, but whose nature is as yet unknown to us.

**The measurement of energy.** Since changes in energy, both from one body to another and from one form into another, are invariably involved in chemical action, it is a matter of great practical importance to devise units for the measurement of

energy and methods for making the measurement. In general each kind of energy must have its own units, just as with matter we have centimeters for lengths, liters for volumes, grams for weights. In some of its forms energy is very difficult to measure directly, and neither units nor methods for the direct measurement of chemical energy have as yet been devised. In such cases it is necessary to transform the energy into a form more convenient for measurement. In the case of chemical energy it is changed into heat or electrical energy, and these are then measured by appropriate units.

**Measurement of heat.** The thermometer measures the *intensity* of heat, — how hot a body is as judged by our sensations of hot

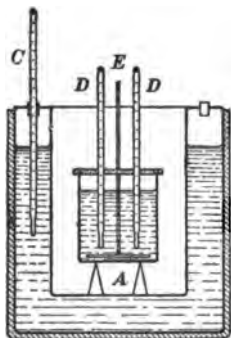


FIG. 2

and cold, — not the quantity of its heat energy. A very fine platinum wire may be readily heated to  $1600^{\circ}$  or above, but the actual heat which it will give out on cooling is very small. The *heat energy* of a body is measured by observing to what extent this body will change the temperature of a given mass of some standard substance. Water has been chosen as the standard, and the unit of heat, called the *calorie* (designated by the abbreviation *cal.*), is defined as the quantity required to change the temperature of one gram of water one degree on the centigrade scale. Sometimes a larger unit is desirable, and this is taken as 1000 times the unit just defined. This is called the large calorie and is designated by the abbreviation *Cal.*

**The calorimeter.** The actual measurement of the quantity of chemical energy transformed into heat in a chemical action is accomplished by the use of an apparatus called the *calorimeter*, one form of which is represented in Fig. 2. The action is arranged to take place in solution in a measured volume of water contained in a thin-walled metal vessel *A*. This is placed within a double-walled vessel *B*, which contains water at the temperature of the room. The thermometer *C* indicates when the water has reached this temperature. This is to prevent the influence of heat from without

and as an added precaution the vessel is covered with a thick layer of non-conducting felt. The heat evolved by the reaction raises the temperature of the solution, the rise being indicated by the thermometers *D, D*. During the reaction the solution is stirred by the stirrer *E*. If the weight of the water is 2570 g. and the rise in temperature is 1.5°, the heat evolved is  $2570 \times 1.5 = 3855$  cal.

**Units of energy.** Some of the units most frequently used in measuring energy, and their relation to each other, are as follows:

- 1 calorie (heat) = 4.189 joules (heat)
- 1 calorie (heat) = 42,720 gram-centimeters (mechanical)
- 1 calorie (heat) = 0.4272 kilogram-meters (mechanical)
- 1 joule (heat) = 1 watt-second (electrical)
- 1 watt-hour = 3600 joules (heat)
- 1 kilowatt-hour = 1.34 horse power

**Relation of matter and energy.** From what has been said about matter and energy it will be seen that we do not have any way of making a fundamental and independent definition of either. We think of these as entirely different in nature because we have not observed matter to disappear and to be replaced by energy, nor energy to be transformed into matter. Yet we cannot imagine either one without the other, and we are really forced to define each in terms of the other. This intimate association of matter and energy points to a very fundamental relation, and we are likely to change our conception of these two things as our knowledge increases. We may even find that the two are really two aspects of the same thing.

### VARIETIES OF MATTER

The variety of forms which matter assumes in all the wonderful transformations of nature is almost infinite, and these may be classified in a great many ways, according to the purpose in view. The interest of the chemist centers chiefly in the composition of substances and in their chemical energy, together with the changes which take place in both of these. From this standpoint he classifies them in three groups; namely, *compounds*, *elements*, and *mixtures*. The distinction can be explained best by some experiments.

**Illustrative experiment 1.** The chief characteristics of the substances iron and sulfur are familiar to almost everyone. Iron filings have the appearance of a heavy black powder, strongly attracted by a magnet. When treated with the liquid known as hydrochloric acid, the iron passes into solution and a colorless gas called hydrogen is evolved, considerable heat being liberated in the process. Sulfur may be obtained as a light yellow powder not attracted by a magnet nor dissolved by hydrochloric acid. It is readily soluble in the liquid known as carbon disulfide, however, which is not true of iron, and when the solution is

allowed to evaporate, the sulfur is deposited in the form of yellow crystals.

When iron and sulfur are thoroughly ground together, a greenish-black powder is obtained which is quite different from either of them; but when we apply the tests which we have found to characterize these two materials it is found

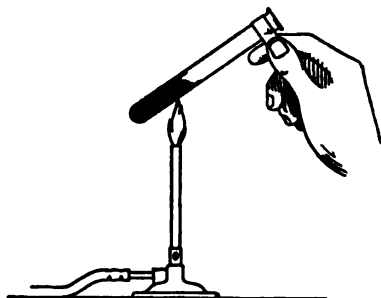


FIG. 3

that in many respects the powder acts like these two taken separately. Hydrochloric acid still dissolves the iron and evolves hydrogen with the same heat as before, leaving the sulfur unchanged. A magnet rubbed through the powder withdraws the iron and leaves the sulfur. Carbon disulfide dissolves the sulfur but not the iron. The sulfur and the iron each act just as they did before they were ground together, and with the same energy.

If now a portion of the mixed powder is placed in a test tube and heated, as shown in Fig. 3, it soon begins to glow at the point of greatest heat, and even if the flame is quickly withdrawn, the glow continues to spread throughout the entire contents of the test tube, and a great deal of heat is set free at the same time. When the product is examined, it is found that many of the characteristics of the iron and sulfur have been modified.

Carbon disulfide no longer dissolves sulfur and leaves iron; a magnet has no effect upon the material; hydrochloric acid dissolves the entire product and evolves a gas of disagreeable odor quite different from hydrogen; the heat liberated by the action of the acid on this material is not the same in quantity as in the case of its action on iron. Many of the properties of this product differ from those of the constituents, among these being density, color, hardness, solubility, and melting point. The material is called iron sulfide.

**Illustrative experiment 2.** When a small quantity of sugar is heated in a test tube, it melts, turns brown in color, gives off vapors, and finally dries up to a solid black residue which is easily identified as carbon. By collecting and examining the vapors it is possible to show that they are largely water. To make this transformation complete it is necessary to apply heat throughout the entire process. In this experiment one substance, merely by the continued application of heat, has given rise to at least two other substances of very different properties, and the change is described as a *decomposition*.

**Chemical reactions.** The two examples which have just been described differ from each other in many ways, but they have several characteristics in common. Most of the properties of the materials concerned undergo a very considerable change, so that it is easy to recognize the fact that the products formed are different from the original materials. A more important characteristic is that the chemical energy of the materials has been changed. The action of iron with sulfur, *when once started*, is attended by the evolution of a great deal of heat which must come from chemical energy present in the iron and sulfur. That the iron sulfide contains less chemical energy than the two original materials is shown by the fact that work must be done upon it to regain the iron and sulfur, and that it is not able to act upon other materials as do iron and sulfur individually.

To effect the decomposition of sugar it is necessary to *supply heat during the entire period of decomposition*, and this heat must

be converted into some other form of energy. A part of it is converted into chemical energy, so that the carbon and the water taken together possess more energy of this kind than did the original sugar. *Any transformation in matter, whether combination or decomposition, which involves a change in the chemical energy of the substances concerned is called a chemical reaction.*

**Definition of chemical compounds.** When it can be shown that a substance is composed of at least two different materials, and that its chemical energy is different from that of the constituents taken separately, it is called a *chemical compound*. Thus we judge iron sulfide to be a chemical compound, for it contains iron and sulfur and yet differs from them in chemical energy. It will be seen that in some cases this difference is so slight that it may be impossible to tell whether there is a real difference or not, especially since it is difficult to measure chemical energy with accuracy, even indirectly. It is therefore not always possible to decide whether a given material is a chemical compound or not. We are assisted in our decision by the fact, to be proved in a later chapter, that the percentage composition of a true compound is always the same. If the material can be obtained in pure form and analyzed, it is usually possible to decide the question in this way.

The above definition is not to be regarded as entirely satisfactory, for it will include all solutions as well as definite compounds. It will serve our purpose at present until the subject of solutions can be taken up in detail.

**Other energy changes involved in chemical action.** Since in a chemical reaction there is always a change in *chemical* energy, it is evident that there must be *other* energy changes as well. Usually the loss or gain in chemical energy is indicated by a corresponding evolution or absorption of heat, as in the experiments with iron sulfide and sugar. Under the proper conditions the chemical energy may be converted into electrical energy. Thus, if a plate of zinc is connected by a wire with one of carbon and the two are dipped into hydrochloric acid, the zinc is acted upon by the acid, and at least some of the chemical

energy set free appears as an electric current in the wire. In other cases it is partially converted into light, as when magnesium wire burns, or into kinetic energy, as when the chemical action of gunpowder imparts motion to the bullet.

It is by no means true, however, that a change in energy may be considered as evidence of chemical action. As we have seen, chemical energy is only one of many forms which may be transformed into the familiar forms of heat and electrical energy. Therefore an energy change in a given case may be due to one or more of many causes other than chemical action. The energy which we observe on turning the key to an electric light is due to the mechanical energy of the engine, which may be driven by water power and involve no chemical action at all. The heat generated when a gas is compressed represents only the mechanical work done upon the gas.

**Conditions affecting chemical action.** There are many conditions which may either promote or hinder chemical action. An increase in temperature is usually favorable to starting chemical action, as was seen in the case of iron and sulfur. It frequently promotes decomposition, as in the case of sugar. Other forms of energy, such as light, mechanical pressure, shock, and electrical energy, may also facilitate either chemical union or decomposition, at times overcoming obstacles which prevent union, in other cases overpowering the chemical attraction which holds a compound together.

**Chemical conduct of substances.** We have seen that substances are characterized by their properties. They are also characterized by the way in which they act toward other substances, as well as by the decompositions which they undergo under various conditions. Thus a substance may burn with a flame when heated in the air, or it may combine with another substance with incandescence, as is the case of iron heated with sulfur. It may decompose when heated, as is true of sugar, or when subjected to the action of the electric current, as does water. It may have no action at all with certain substances under

ordinary circumstances, while with some of them it may combine at high temperatures and with others remain indifferent. All such peculiarities are collectively called the *chemical conduct* of a substance. It will be seen that such conduct usually depends upon the presence of other materials, as well as upon the physical conditions which prevail, such as temperature and pressure.

**Elementary substances, or elements.** The experiments just described suggest that it will be interesting if we heat iron, sulfur, water, and carbon to see whether any new substance can be obtained through their decomposition.

Experience has shown that in many cases decompositions may be brought about by the electrical current or by the action of substances possessed of great chemical energy, and we may also employ these methods. In such ways chemists have succeeded in decomposing water into two invisible gases, oxygen and hydrogen, so that it must be regarded as a compound.

The other three substances, carbon, iron, and sulfur, have never been decomposed, notwithstanding the many efforts directed to this end. Substances like these three, which have never been decomposed into two or more different materials, are called *elementary substances, or elements*.

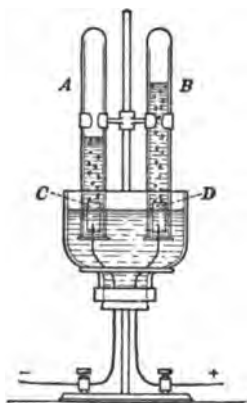


FIG. 4

**The decomposition of water.** The decomposition of water may readily be observed by the aid of an apparatus such as that represented in Fig. 4. Two test tubes (A and B) are filled with water and inverted in a vessel half filled with water to which a little sulfuric acid has been added. A piece of platinum foil (C and D) attached to a wire is then brought under the end of each tube. When these wires are connected with a source of current supplying from 6 to 10 volts, bubbles of gas will be seen to form in each tube. These gases may be shown to have different properties; they are hydrogen and oxygen. The reason for adding the sulfuric acid cannot be explained at this time, but will be discussed later.

**Elements not simple units.** In recent years it has been demonstrated that, in some way which we do not understand, the elements themselves have been formed by the condensation of two really primitive units, namely, positive and negative electricity. The positive electrical unit is closely related to the two gases hydrogen and helium, and a few of the elements, such as uranium and thorium, are very slowly decomposing, yielding helium in the process. Tremendous energy is liberated in this decomposition, and when exposed to this energy some well-known elements, such as nitrogen, are knocked to pieces, yielding helium. But, so far as we know, all the so-called elements remain unchanged by any ordinary process of nature as well as during chemical combination or decomposition, and so for all practical purposes we may regard them as the unchanging units out of which all compounds are built up.

**Number of the elements.** While many thousands of compounds have been described, the number of the elements at present known is comparatively small, that is, eighty-seven. For reasons to be explained later, chemists are reasonably certain that the total number of elements is ninety-two. Only five, therefore, remain to be discovered. Some of these elements have long been known; others have only recently been discovered. The last one announced is *hafnium*, which was first described as an element in 1923. A complete list of the known elements is given in the table in Appendix B.

Following the name of each element in the table is an abbreviation called a *symbol*, by which the element is designated among chemists. The symbol is usually the initial letter of the name of the element, together with some other characteristic letter. In the case of some of the elements the symbol is the abbreviation of the old Latin name, as is true of iron (*ferrum*), gold (*aurum*), and mercury (*hydrargyrum*). The significance of the column of numbers will be made clear a little later.

**Distribution of the elements.** So far as we can judge, the elements are of very unequal occurrence in nature. It must be remembered, however, that our knowledge of the earth's composition is confined to what is comparatively a very thin surface shell, not exceeding a few miles in thickness. Relative to the diameter of the earth this shell is not thicker than is the skin

on a large apple. The table on page 17, prepared by F. W. Clarke and based on the analysis of representative rocks and minerals, gives an estimate of the composition of this shell. It will be seen that 20 of the elements are estimated to constitute 99.5 per cent of the shell, the other 63 together making up the remaining 0.5 per cent. Some of the elements are of such rare occurrence that only a few grams have ever been isolated.

**Elements essential to life.** A careful examination of the materials present in living organisms shows that only a limited number are of vital importance to us. The following table, compiled by Sherman, indicates the average composition of the human body. It is possible that other elements have an importance which we do not realize, but, so far as we can judge, these are the only ones upon which living organisms are dependent.

#### AVERAGE COMPOSITION OF THE HUMAN BODY

Oxygen . . . 65.00%	Phosphorus . . 1.00%	Magnesium . . 0.05%
Carbon . . . 18.00%	Potassium . . . 0.35%	Iron . . . 0.004%
Hydrogen . . 10.00%	Sulfur . . . 0.25%	Iodine . . . traces
Nitrogen . . . 3.00%	Sodium . . . 0.15%	Fluorine . . . traces
Calcium . . . 2.00%	Chlorine . . . 0.15%	Silicon . . . traces

**Mixtures.** It is quite possible to prepare, from either elements or compounds, or both, a body which is not itself a compound but is merely a *mixture*. Ordinary concrete is such a material, for in a broken piece it is easy to identify the crushed stone, the sand, and the cement which compose it. Granite is a sort of natural concrete, in which two very different-looking crystalline materials, mica and feldspar, are bound together by a glassy substance called silica. A crystal of mica broken out from granite has exactly the same chemical energy as does a pure crystal obtained from any other source. Iron and sulfur when rubbed together form a material more closely resembling a compound, in that it is apparently of even quality throughout, or is homogeneous. An examination under the microscope shows that this is not really so, for the particles of iron and sulfur can

still be seen lying side by side unchanged. It will be convenient to make use of the term *components* in designating the distinct materials in a mixture.

In many cases the two types, mixtures and compounds, approach so nearly to each other that it is impossible to distinguish between them. For example, alcohol and water mix

CLARKE'S TABLE

	SOLID SHELL 93 PER CENT	OCEAN 7 PER CENT	AVERAGE INCLUDING ATMOSPHERE
Oxygen . . . . .	47.33	85.79	50.02
Silicon . . . . .	27.74		25.80
Aluminium . . . . .	7.85		7.30
Iron . . . . .	4.50		4.18
Calcium . . . . .	3.47	0.05	3.22
Magnesium . . . . .	2.24	0.14	2.08
Sodium . . . . .	2.46	1.14	2.36
Potassium . . . . .	2.46	0.04	2.28
Hydrogen . . . . .	0.22	10.67	0.95
Titanium . . . . .	0.46		0.43
Carbon . . . . .	0.19	0.002	0.18
Chlorine . . . . .	0.07	2.07	0.20
Bromine . . . . .		0.008	
Phosphorus . . . . .	0.12		0.11
Sulfur . . . . .	0.12	0.09	0.11
Barium . . . . .	0.08		0.08
Manganese . . . . .	0.08		0.08
Strontium . . . . .	0.02		0.02
Nitrogen . . . . .			0.03
Fluorine . . . . .	0.10		0.10
Other elements . . . . .	0.50		0.47
	100.00	100.00	100.00

in all proportions to form a perfectly homogeneous liquid copper and zinc when melted together form brass, which in properties is quite different from either, yet has no fixed percentage composition. A perfectly definite compound, such as water, may be regarded as standing at one end of a series, with an undoubted mixture like granite at the other. There is every gradation between these two extremes, and in the middle of the

series the one type changes by almost imperceptible stages into the other. In the majority of cases the distinction is easily made, and it affords a useful basis of classification.

**Plan of study.** We shall now take up the study of two abundant and typical elements, namely, oxygen and hydrogen, and following this a consideration of the compounds which they form with each other. This will serve to emphasize the characteristics of chemical action, and provide a basis for the consideration of other elements and their compounds.

### QUESTIONS

1. (a) Explain what is meant by the heat equivalent of chemical energy; (b) by the mechanical equivalent of electrical energy.
2. When a drill cuts a hole in a piece of iron, where does the heat come from that makes the drill hot?
3. Does the ordinary form of balance measure mass or weight?
4. What are the conditions that favor the chemical reaction in (a) lighting a match? (b) setting off dynamite? (c) taking a photograph?
5. How many reasons can you give for considering the change of a mixture of iron and sulfur into iron sulfide to be a chemical reaction?

### PROBLEMS

1. The absolute density of air is 0.0012928. What is its density referred to oxygen as 16? (See Appendix B for data.)
2. In a reaction involving 100 g. of material, 2700 g. of water is heated from 18.4° to 21.6°. (a) What is the heat evolved per kilogram of material? (b) How many kilogram-meters of work would the latter equal?
3. 1 g. of anthracite coal when burned evolves about 7300 cal. of heat. (a) What weight of it will be required to heat 4 l. of water from room temperature (20°) to the boiling point supposing that all the heat is available? (b) How many watt-hours of electrical energy would this equal?
4. How much of the coal described in problem 3 will be required to produce 10 kilowatt-hours of electrical energy?

## CHAPTER II

### OXYGEN

**History.** Joseph Priestley, an English clergyman and investigator, is usually regarded as the discoverer of oxygen. In 1774, in the course of some experiments with gases, or "airs," as he called them, it occurred to him to try the effect of heat upon certain solids, to determine whether any gas is liberated in this way, and, if so, to collect the gas and study its properties. He placed in a glass tube a small amount of the compound now known as mercuric oxide, and heated it by means of a large lens used as a burning glass. He found that under these conditions a colorless gas was set free, which aroused his interest, because "a candle burned in this air with a remarkably vigorous flame." It is now known that the Swedish chemist Scheele had obtained this same gas a year earlier by heating niter as well as the mineral pyrolusite, but Priestley was the first to publish the results of his experiments, and it was through his description of the gas that it became known to scientists.

At the time of Priestley's discovery the renowned French chemist Lavoisier, whose life was later sacrificed in the French Revolution, was engaged in a study of the nature of combustion, and at once he became greatly interested in this newly discovered gas. He found that a number of elements such as phosphorus and sulfur unite with it to form compounds which were at that time regarded as acids. Believing that the characteristic properties of acids were due to the presence in them of this substance, he proposed for it the name *oxygen*, a word derived from the Greek and meaning "acid former." We now know that this name is not appropriate, since many acids do not contain oxygen.

It is of interest to know that Priestley, because of his religious views, was compelled to leave England and settled in Northumberland, Pennsylvania. The house in which he lived has been purchased by a group of persons interested in the history of chemistry, and it will be preserved as a suitable memorial to Priestley.

**Occurrence.** Oxygen occurs in nature both as free oxygen and as a constituent of many compounds. In 100 volumes of dry air there are approximately 21 volumes of the free element. In the combined state it constitutes 88.81 per cent by weight of water and nearly one half by weight of the common minerals such as limestone, sandstone, granite, and clay, which together make up the earth's crust. It is also an essential constituent of the compounds present in living organisms. For example, nearly two thirds of the human body is oxygen (see table, p. 16). The total weight of oxygen in the land, the water, the atmosphere, and in living organisms may be regarded as roughly equal to the united weights of all the other elements.

**Preparation.** Since oxygen is so abundant and is present in such a large variety of compounds, it is easy to understand why many different methods may be used in obtaining it in pure condition. The most important of these methods are the following:

1. *By heating certain compounds of oxygen.* Many compounds containing oxygen give off at least a portion of it when heated. For example, mercuric oxide and potassium chlorate — compounds which contain respectively 7.4 per cent and 39.2 per cent of oxygen — give off all their oxygen when heated to a moderately high temperature. Other compounds, such as manganese dioxide and barium peroxide, give up only a definite fraction of their oxygen.

2. *By the decomposition of water by means of an electric current.* It will be shown in a later chapter that water is a compound consisting of 88.81 per cent oxygen and 11.19 per cent hydrogen. When pure it is practically a nonconductor of electricity, but if a little sulfuric acid or potassium hydroxide is added to it, the resulting solution very readily conducts the current. In this

process a series of changes take place which result in the decomposition of the water into its constituents. This decomposition of a compound through the agency of an electric current is commonly referred to as *electrolysis*.

**Apparatus.** Fig. 5 represents a convenient form of apparatus for effecting the electrolysis of water in this manner. Two platinum wires (*A* and *B*), each with a small piece of platinum foil known as an *electrode* attached to one end, are fused through the tubes *C* and *D*, as shown in the figure. The stopcocks at the tops of these tubes are opened, and water, to which has been added about one tenth of its volume of sulfuric acid, is poured into the tube *E* until the side tubes *C* and *D* are completely filled. The stopcocks are then closed. The platinum wires are now connected with a battery capable of supplying about 6 volts (3 storage or 6 ordinary dry cells joined in series). The current flows through the acidulated water from one electrode to the other, and brings about the decomposition of the water into its constituents. The oxygen rises in bubbles from the positive electrode and collects in the upper part of tube *C*, while the hydrogen rises from the negative electrode and collects in tube *D*.

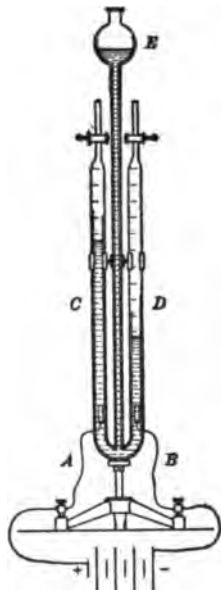


FIG. 5

3. *By separation from air.* Since air contains such a large percentage of free oxygen, one would naturally expect methods to be devised for obtaining it from this source.

The problem is not as simple as it may seem, for there are other gases in the air, and the separation of a gas in a pure condition from a mixture of gases is always difficult. In this case it may be accomplished by either of two methods:

(a) *Chemical method.* A few substances are known which when heated in the air to a temperature varying with the nature of the substance combine with oxygen present in the air, but give it up once more at a higher temperature. Barium oxide, a compound containing 10.43 per cent of oxygen, is a good example of this kind. When heated in the air to a temperature of

about 500°, it combines with oxygen and is thereby changed into barium peroxide, a compound which contains 18.89 per cent of oxygen. When this is further heated to about 1000°, the additional oxygen is set free once more and may be collected, the barium peroxide being at the same time changed into the oxide again. These transformations may be represented thus:



The arrows indicate that the reaction may proceed in either direction, according to the temperature.

(b) *Mechanical method.* By subjecting air to the combined effects of pressure and very low temperature it is possible to obtain it in the form of a liquid which is essentially a mixture of oxygen and nitrogen in the liquid state. If this liquid is allowed to stand under ordinary pressure, the nitrogen (being more volatile than the oxygen) rapidly vaporizes and is thus separated from the oxygen, which vaporizes later. It is thus possible to obtain both oxygen and nitrogen in a pure state from the air, and this method serves as an inexpensive one for the preparation of these gases on a large scale.

**Practical methods of preparation.** With these general methods of preparation before us, we may make a selection of those best suited to the actual preparation of the gas. For the purpose of laboratory experiments, in which relatively small quantities are desired, the choice will naturally be guided by convenience and simplicity of apparatus, while in the preparation on a commercial scale economy will determine the method.

**Laboratory method.** The method usually chosen for preparing oxygen in the laboratory consists in heating potassium chlorate, which is a white, solid compound of potassium, chlorine, and oxygen. The evolution of the gas becomes marked at about 400°, and if the heating is continued long enough, all the oxygen present in the chlorate is liberated. It is a remarkable fact that the rate at which the oxygen is evolved at any given temperature is greatly increased by the presence of small quantities

of certain substances, notably manganese dioxide. By mixing such a substance with the chlorate it is possible, therefore, to expel the oxygen rapidly at a lower temperature than would otherwise have to be employed.

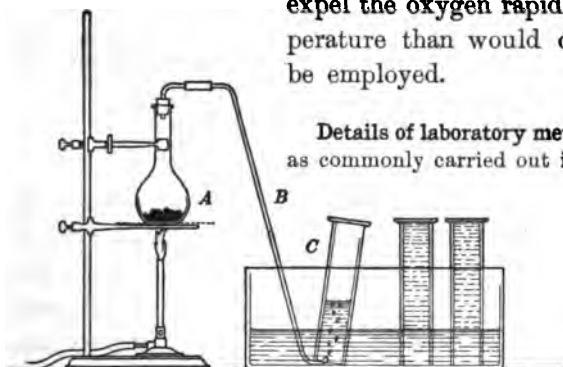


FIG. 6

**Details of laboratory method.** The operation, as commonly carried out in the laboratory, is as follows: The potassium chlorate, mixed with about one fourth of its weight of manganese dioxide, is placed in a suitable vessel, such as a glass

flask, which is provided with a cork and glass tube, as shown in *A* (Fig. 6). Upon applying a gentle heat, oxygen is evolved and passes out through the tube *B*. It is evident that the oxygen at first escaping is mixed with the air contained in the flask. In a short time, as the evolution of oxygen continues, all this air is displaced, and the pure oxygen may then be collected by bringing the end of the delivery tube under the mouth of a glass cylinder *C*, which has been filled with water and inverted in a trough of water, as shown in the figure. The gas rises in the cylinder and displaces the water. In preparing larger quantities of oxygen a copper retort (Fig. 7) having a capacity of from 500 to 1000 cc. may be used to advantage in place of the more fragile glass flask.

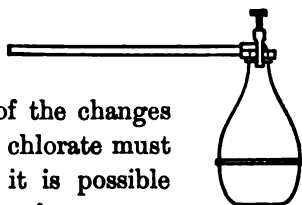


FIG. 7.

Although the complete discussion of the changes which take place on heating potassium chlorate must be postponed until a later chapter, it is possible at this time to state in a general way what occurs. The composition of potassium chlorate is as follows: potassium, 31.9 per cent; chlorine, 28.9 per cent; oxygen, 39.2 per cent. When the substance is heated, a series of changes occur which finally result in the liberation of all the oxygen and the formation of a white, solid compound of potassium and chlorine, known as potassium chloride. These facts may be

expressed by the following method, in which the names of the elements present in each compound are given in brackets just below the name of the compound:

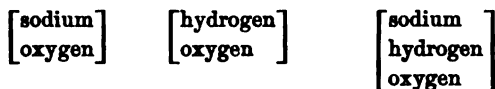
potassium chlorate  $\longrightarrow$  potassium chloride + oxygen



As to the way in which the manganese dioxide promotes the decomposition, it may be said at once that we do not know. Apparently it undergoes no change during the reaction. Certainly it contributes no oxygen, for the weight of the latter obtained is always 39.2 per cent of the weight of the chlorate used, irrespective of the presence of manganese dioxide. This is but one example of many in which the rate of change is influenced by an apparently inactive substance. Such materials are called *catalytic agents*, or *catalyzers*, and we shall meet with them frequently in subsequent pages.

A more convenient, although more expensive, method for preparing oxygen in the laboratory consists in adding water to sodium peroxide. These two substances, when brought in contact with each other, react in such a way as to liberate oxygen. At the same time there is formed a white solid compound, consisting of sodium, hydrogen, and oxygen, known as sodium hydroxide:

sodium peroxide + water  $\longrightarrow$  sodium hydroxide + oxygen



**Apparatus.** A convenient form of apparatus for generating oxygen by this method is shown in Fig. 8. The peroxide is placed in the flask *A* while the bulb of the separatory funnel *B* is filled with warm water. The stopcock *C* is then turned until the water enters the flask drop by drop. As soon as the water comes in contact with the peroxide, oxygen is evolved, which escapes through *D* into the adjoining bottle; after bubbling through the water in the bottle, it passes out and is collected by the usual method.

**Commercial preparation.** A number of methods for the preparation of oxygen on a large scale have been employed at different times. In the United States, at the present time, practically

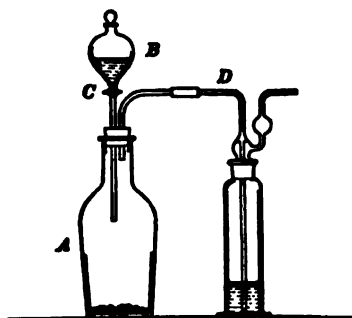


FIG. 8

all of the oxygen prepared for commercial purposes is obtained either from liquid air or by the electrolysis of water. The resulting oxygen is pumped into strong steel tubes under great pressure (Fig. 9), and in this form is an article of commerce.

**Properties.** Under ordinary conditions, oxygen is a colorless, odorless,

and tasteless gas. At  $0^{\circ}$  and under a pressure of 1 atmosphere 100 cc. of water dissolves 4.89 cc. of the gas, so that it is not very soluble and may be collected over water with little loss. One liter of oxygen, measured at  $0^{\circ}$  and under a pressure equivalent to that of a column of mercury 760 mm. in height (the normal barometric pressure at the sea level), weighs 1.429 g. Since 1 l. of air under the same conditions weighs 1.2928 g., it will be seen that oxygen is 1.105 times as heavy as air.

Through the combined effect of pressure and low temperature oxygen may be obtained in the form of a liquid. To accomplish the liquefaction the temperature must be at least as low as  $-118^{\circ}$ , at which temperature a pressure of 50 atmospheres is required (see critical temperature, p. 94). At still lower temperatures less pressure will suffice. Liquid oxygen has a slightly bluish color and boils at  $-183^{\circ}$  under a pressure of 1 atmosphere. By cooling this liquid to an extremely low temperature, Dewar, an English investigator, succeeded in freezing it to a snowlike solid which melts at  $-218^{\circ}$ .

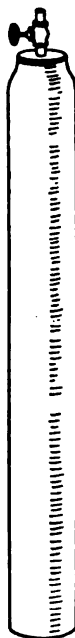


FIG. 9

**Chemical conduct.** At ordinary temperatures oxygen is only a moderately active element—a fact which may be inferred from our experience that very few of the materials coming under common observation are acted upon by the oxygen of the air with noticeable rapidity. With rise of temperature it becomes very much more active. At ordinary temperatures for example, the elements sulfur, iron, and carbon are not noticeably acted upon by oxygen, while in the case of phosphorus the action, though slow, is quite apparent. If now the temperature of each of

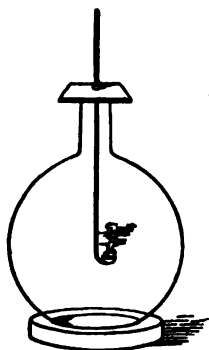


FIG. 10

these elements is slowly raised, the reaction becomes more marked and the phosphorus soon bursts into flame. At higher temperatures the sulfur, carbon, and iron likewise are ignited. If each of the elements, as soon as ignited in the air, is introduced into a vessel of pure oxygen (Fig. 10), the action becomes much more energetic. The pale blue flame of the burning sulfur is greatly increased in size and brightness, the iron throws off countless sparks, while the phosphorus and carbon burn with dazzling brilliancy. In each case the action increases in intensity as it progresses. Many compounds act in the same general way. Thus wood, coal, oil, fats, and natural and artificial gas all burn readily in air and more brilliantly in pure oxygen. Indeed, there are but few elements which will act upon so many other elements and compounds as does oxygen.

This general conduct suggests a great many questions. What becomes of the materials when they burn? Why is there a difference in the ease of ignition? Why do not all substances burn? Why is the action more intense in oxygen than in the air, and why does it become more energetic and brilliant as it progresses? To some of these questions we can find an answer at once; others will occur again many times in our study and in the end will remain only partially answered.

The nature of the action of oxygen upon substances; oxidation; oxidizing agent. By means of experiments it is possible to show that the action of oxygen upon another element consists in the union of the two elements to form a compound. Thus, when sulfur burns in oxygen, both sulfur and oxygen disappear as such, and in their place we find a gaseous compound composed of the two elements. Likewise, when phosphorus, iron, and carbon burn in oxygen, there are formed compounds of these elements with oxygen. The action of oxygen upon compounds is similar to its action upon elements, and consists in the union of oxygen with one or more of the elements present in the compound, or, in some cases, with the compound as a whole. Thus, when the gaseous compound of hydrogen and sulfur known as hydrogen sulfide burns in a limited supply of air, only the hydrogen present combines with the oxygen, while the sulfur is set free. If the supply of air is sufficient, however, to furnish the necessary oxygen, then both the hydrogen and sulfur combine with the oxygen.

When any substance or its constituent parts combines with oxygen, the substance is said to *oxidize* and the process or change which takes place is called *oxidation*. Thus we say that phosphorus readily oxidizes, or that it easily undergoes oxidation. Oxidation may be brought about by the use of oxygen or of some compound, such as potassium chlorate or sodium peroxide, that will readily supply oxygen. When so used, the oxygen itself or the compound which furnishes the oxygen is called the *oxidizing agent*. It will be pointed out in the appropriate place that the use of the term *oxidation* is not confined to such changes as those mentioned above but has a much broader application, even including certain changes in which no oxygen takes part. For the present, however, the term will be used in the sense explained above.

**Oxides; products of oxidation.** When any element combines with oxygen, the resulting compound is known as an *oxide* of that element. Thus the compound formed by the union of sulfur

with oxygen is known as an oxide of sulfur. Likewise, when phosphorus, iron, and carbon combine with oxygen, the resulting compounds formed are oxides. The particular oxide or oxides formed in the oxidation of any substance are known in general as the *products of oxidation* of that substance.

Most of the elements form oxides; indeed some of the elements form more than one oxide, as is the case with barium, to which reference has already been made (p. 21). Some of the oxides are invisible gases, as is true of the oxides of sulfur and carbon, formed when these two elements burn in air or in pure oxygen. In a few cases the oxide is a liquid, the most familiar example being water, which is an oxide of hydrogen. In the great majority of cases, however, the oxides are solids.

**Weight relations in oxidation.** If it is true that oxidation is essentially the union of oxygen with other elements or compounds, it must necessarily follow that the weight of the product formed is greater than that of the substance oxidized or burned, although our common experience with fuels would hardly lead us to such a conclusion. That the weight does increase may be demonstrated by arranging an experiment in which the oxidation takes place on one pan of a balance. For example, some powdered iron may be placed in a small porcelain dish and accurately counterpoised on the balance. The iron may then be ignited by directing a hot flame upon it. As the oxidation proceeds, it will be seen that the scale pan supporting the dish sinks. A modification of this experiment will show a similar gain in weight during the burning of a candle.

The candle is arranged on a balance pan shown in Fig. 11. Over it is suspended a wide glass tube (a lamp chimney) loosely filled with sticks of sodium hydroxide, a substance which will absorb both water and oxide of carbon. When the whole apparatus has been brought to an equilibrium on the balance, the candle is lighted. As it burns, the materials of which it is composed (chiefly hydrogen and carbon) are oxidized, forming oxide of hydrogen (water) and of carbon, which are drawn up through the chimney and absorbed by the sodium hydroxide. The balance pan sinks as the oxidation progresses, indicating an increase in weight.

Such experiments as these have been carried out with the greatest care by skillful workers, and it has been shown that the weight of the material oxidized, plus that of the oxygen used up, exactly equals the weight of the products of the oxidation.

**Heat, temperature, and light in oxidation.** In the burning of the elements we have been considering, as well as of such familiar fuels as wood, coal, and oil, it is noticed that at first the heat given off does not seem to be very great, and the light is quite feeble. As the oxidation proceeds, the temperature rises quite rapidly and the light grows brighter, in some cases becoming almost blinding. This conduct is readily understood if we keep clearly before us the relation between heat, temperature, and light.

By *heat* we refer to a definite *quantity* of one form of energy, namely, heat energy, and we measure this in calories (p. 8).

By *temperature* we mean the *intensity* of this energy, and this

we measure by a thermometer. An illustration will make the distinction clearer. Let us suppose a given weight of some material to contain 100 cal. of heat. If now heat is applied to this material until another 100 cal. is added to it, the weight of the material remains constant, while the quantity of heat is doubled. The quantity of heat associated with a given weight of matter has been increased, and we say that the intensity is greater, this being indicated by a higher temperature. If, however, we add to the material containing 100 cal. of heat an equal weight of the same material, also containing 100 cal., the quantity of heat is doubled, but the quantity of matter is doubled at the same time. In this case the intensity remains unchanged, and the temperature is the same as before.

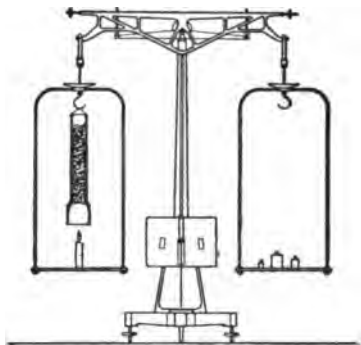


FIG. 11

Accordingly, when chemical energy is changed into heat in the process of oxidation, under conditions such that the loss through radiation and conduction is small, all the materials concerned in the reaction have large additions to their heat energy, and their temperature consequently rises. At high temperatures (depending on the nature of the materials) a part of this heat is changed into light energy, the transformation being greater the higher the temperature. Increasing brightness is therefore an indication of rising temperature.

**Exothermic and endothermic reactions.** When such a substance as carbon, sulfur, or phosphorus burns in oxygen, heat is evolved, the exact amount depending upon the nature of the substance. Thus, when carbon burns in oxygen, 8088 cal. are liberated for each gram of carbon burned, while under similar conditions one gram of sulfur will liberate 2217 cal. All such reactions in which heat is liberated are known as *exothermic reactions*.

In many other reactions heat is absorbed and must be supplied from an external source if the action is to continue. Thus, if we wish to decompose mercuric oxide into mercury and oxygen we must apply heat continuously, otherwise the reaction will cease. For example, to decompose one gram of mercuric oxide requires 141 cal. Moreover, the heat applied must be above a certain intensity or temperature. This heat is stored up as chemical energy in the resulting mercury and oxygen. All such reactions which take place only with absorption of heat are known as *endothermic reactions*.

**Combustion.** When a reaction proceeds rapidly enough to produce light, it is called *combustion*. Naturally such reactions are exothermic in character. The most familiar examples of combustion are those in which substances burn in air or oxygen; but we shall meet with cases of combustion in subsequent pages in which there is no oxygen taking part in the reaction. Ordinarily, however, when we speak of a combustible substance, we mean one that will burn in air or oxygen.

**Incombustible substances.** The question naturally rises, Why do not all substances burn? In the case of many substances, such as the compounds formed in combustion, the answer is very evident, for they already contain all the oxygen with which they are capable of uniting, at least under the conditions which prevail during combustion. Many oxides, such as water, are of this class, as well as most of the substances which constitute the solid crust of the earth. The materials of which fireproof buildings are made—brick, tile, cement, plaster, asbestos—are also of this character. Some of the metals, like iron, will burn, but only at such high temperatures that they are practically incombustible under all ordinary conditions unless they are in a finely powdered form. Other substances, however, such as the elements fluorine and argon, do not combine with oxygen under any known condition.

**Spontaneous combustion.** It has been found that the rate at which oxidation goes on is greatly increased by raising the temperature of the material undergoing oxidation. Consequently, if the conditions surrounding oxidation are such that the heat given off cannot escape, the temperature will steadily rise, and because of this the rate of oxidation will increase. The increased heat thus set free will still further raise the temperature, until the oxidation passes into active combustion, the point at which this occurs being called the *kindling temperature*. Materials taking fire in this way are said to undergo *spontaneous combustion*. It will be seen that the essential conditions are (1) an existing slow oxidation and (2) good heat insulation. Linseed oil, used in paints, undergoes rather rapid oxidation in air, and oily rags left by painters not infrequently occasion disastrous fires. Fine coal in the center of a heap or in the closed hold of a vessel sometimes takes fire. Almost any finely divided combustible material, such as sawdust or flour, is dangerous when stored in a warm dry place. Sometimes the heat of fermentation, which is a kind of oxidation, will start a fire in a haystack or barn if the hay is not well dried before being stored.

**Slow oxidation.** More frequently the heat set free when substances slowly oxidize in the air is conducted away about as fast as it is liberated, so that the temperature does not greatly change. These slow oxidations are often of great economic importance. Most of the metals slowly rust in the air, and in some cases this process is simply one of oxidation, the product being an oxide of the metal. In other cases, as with iron, the reaction is more complex, since water takes part in it and the rust contains hydrogen as well as oxygen and the metal.

Many of the changes involved in the various processes of growth and decay of organisms belong to this same class of slow oxidations. The oxidation of the food which we eat keeps the body at the most efficient temperature. Broken-down tissue is changed by oxidation into forms in which it can be easily eliminated from the body. Much of the refuse matter from organisms, which would soon become a nuisance if not a danger to health, is oxidized for the most part into water and oxide of carbon, both of which are again absorbed by growing plants. It is a very wonderful adjustment by which all these processes work in harmony with each other.

**Speed of oxidation.** The description of the conditions which lead to spontaneous combustion has already made it clear that a given oxidation may take place at very different rates. It is rather natural to infer that when the oxidation of a definite weight of any substance proceeds very slowly, less heat is evolved than when it proceeds rapidly, for in the latter case a much higher temperature is reached. Very exact measurements have shown that such an inference is wrong; the total heat evolved in the two cases is precisely the same irrespective of the rate, provided only that the same products and the same weight of them are formed. It is also true that in general the same products are formed, though this is not always so.

It is a matter of much interest for us to inquire what conditions influence the rate or speed of a reaction, *the speed being*

*measured by the weight of material undergoing change in a unit of time.* Such knowledge will have much practical value, for in various industrial processes increase of speed of reaction means great saving of time. In the purchase of fuel it is the heating value we really pay for, and sometimes we wish to use this so as to get as much heat as possible in a short time, while for other purposes we may desire to obtain the heat slowly but evenly.

**Conditions which influence the speed of oxidation.** For the present we need consider only three factors which affect the speed of oxidation.

1. *Effect of temperature.* The most obvious influence affecting the speed of oxidation is temperature. At a high temperature oxidation takes place rapidly; as the temperature is lowered the speed decreases, until at ordinary temperatures it may be impossible to detect any action whatever. It is exceedingly improbable, however, that the process entirely ceases; it merely becomes so slow that we have no means of detecting any change.

2. *Effect of concentration.* It is evident that anything which increases the quantity of oxygen in contact with the surface of the burning substance will tend to hasten the reaction. One reason why substances burn more rapidly in oxygen than in air is that the latter is only one fifth oxygen, so that a body burning in air is at one time in contact with only one fifth as much oxygen as when it is burning in the pure gas. Instead of increasing the concentration of the oxygen we may often hasten the oxidation by extending the surface of the solid substance. A log of wood burns more slowly than the same wood split into kindling. A lump of coal burns rather slowly, but when finely powdered and suspended in the air as dust, it burns almost instantaneously, and with explosive violence.

3. *Catalysis.* We have already seen that potassium chlorate gives up its oxygen much more rapidly under the catalytic influence of manganese dioxide than when heated alone. In a similar way the speed of oxidation may sometimes be increased by the

action of some suitable catalytic agent. Thus, when the oxide formed in the combustion of sulfur (called sulfur dioxide) is heated with oxygen under the proper conditions, it slowly takes up an additional quantity of oxygen to form a new compound known as sulfur trioxide. It has been found that the speed of this oxidation may be greatly increased by the presence of certain catalytic agents, such as finely divided platinum, and this discovery has led to marked improvements in the manufacture of sulfuric acid. In like manner the presence of a trace of moisture greatly increases the speed of oxidation of many substances.

**Importance of oxygen.** The great importance of oxygen in nature is evident from the facts which have already been presented in this chapter. It is a constituent of the great majority of the compounds which collectively constitute the solid earth, the living creatures upon it, and the water which covers so much of its surface, while the atmosphere is a great reservoir from which a supply of the free element can be drawn at any time.

Free oxygen is essential to the life of all organisms, with the exception of some of the lowest forms. Aquatic animals obtain the necessary oxygen from the air dissolved in the water in which they live. Free oxygen also plays a prominent part in the decomposition of refuse matter which collects on the surface of the earth, much of it being oxidized into harmless gases. It is noteworthy, however, that the oxidation of such matter takes place only in the presence of certain minute forms of living organisms known as bacteria.

Pure oxygen is used chiefly (1) for burning out the carbon deposited in the cylinders of gas engines and (2) as a source of heat in the cutting and welding of metals. Smaller quantities of oxygen are used in the preparation of certain of its compounds, as well as for the treatment of those diseases in which the patient is unable to inhale sufficient air to supply the necessary quantities of oxygen. Aviators are supplied with the pure gas for use at high altitudes.

**The definiteness of chemical processes.** Throughout this chapter attention has been repeatedly directed to the fact that chemical processes involve definite weights of matter. For example, the composition of a number of compounds has been expressed in exact percentages, since experiment has shown that these always have precisely the composition stated, irrespective of the source from which they are obtained or the method by which they are prepared. After extensive investigation of a very large number of compounds, chemists have concluded that this constancy of composition is a characteristic of every true compound, and a statement of this characteristic is commonly called the law of definite composition.

In like manner the chemical reactions which compounds undergo are always perfectly definite under stated conditions. Thus, when potassium chlorate is heated, for every 100 g. decomposed there result 39.2 g. of oxygen and 60.8 g. of potassium chloride. When iron burns in oxygen, 100 g. of iron combines with 38.20 g. of oxygen to form 138.20 g. of oxide of iron. If less than 38.20 g. of oxygen is present, then a corresponding amount of iron will remain unchanged. On the other hand, if more than 38.20 g. of oxygen is present, then all the iron will be changed into the oxide, and the excess of oxygen will remain unaltered. The actual experiments which justify these conclusions will come before us from time to time as we proceed.

**The phlogiston theory of combustion.** Before leaving the topic of combustion it will be of interest to contrast our present ideas with those of the chemists of a few centuries ago, or of the alchemists, as they were sometimes termed. Of the many conceptions which have been held at different times, that which is known as the phlogiston theory had by far the greatest influence upon the development of chemistry. This theory was advanced by Becher (1635-1682) and was greatly extended and developed by the distinguished German professor Stahl (1660-1734). According to this theory every combustible substance contains more or less of a material, or "principle," called phlogiston, the escape of which constitutes combustion. The ash remaining represents the original substance minus phlogiston. Substances which leave no ash are nearly pure phlogiston.

When it is remembered that at that time gases were little understood, oxygen unknown, and heat and light regarded as material substances given off during combustion, and that in this process something very evidently did escape (namely, the gaseous oxides), it will be seen that the theory was a reasonable one. It was known that metals increased in weight during combustion, but little importance was at that time attached to weight relations, and some adherents of the theory even assumed that phlogiston had negative weight, that is, weighed less than nothing. It was also difficult to explain why combustion required the presence of air. The theory was almost universally held for a hundred years, and was given up only after oxygen had been discovered and Lavoisier had demonstrated the true nature of combustion. Even then some chemists did not accept the new ideas.

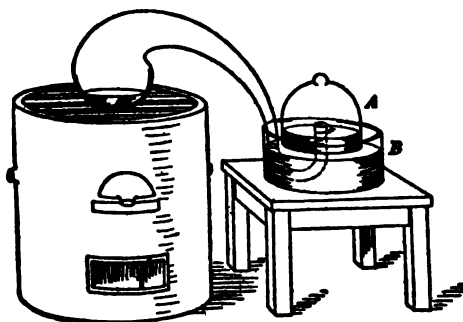


FIG. 12

Priestley, whose discovery of oxygen contributed so much to the true explanation of combustion, never gave up the phlogiston theory. In fact, one of his last publications was entitled "The Doctrine of Phlogiston Established."

The demonstration of the true nature of combustion must be regarded as one of the greatest achievements in the history of

chemical science, for our modern views date from it. It is therefore worth while to learn something of the methods which Lavoisier employed. Fig. 12 shows the form of apparatus used in one of his most important experiments. A bell jar *A* full of air was placed on a basin of mercury *B*, and a retort was arranged in such a way that its delivery tube passed under the edge of the bell jar and communicated with the included air. Lavoisier placed 4 oz. of mercury in the retort and heated it for 12 days. As the heating progressed, he observed that the mercury was gradually converted into a red solid (oxide of mercury) and that this change was attended by a contraction in the volume of the air in the bell jar, as shown by the rise of mercury in it. The contraction amounted to from 7 to 8 cu. in. He then placed the red solid in a small retort and decomposed it by heating it to a higher temperature, obtaining the original mercury once more, together with from 7 to 8 cu. in. of oxygen. He also determined the weight relations of the several substances taking part in these changes, and was able to prove that when tin is heated in contact with the air, it combines with oxygen, and that the increase in weight is equal to that of the oxygen

absorbed. In addition to these experiments, Lavoisier burned phosphorus in a limited amount of air confined over mercury and found that only a portion of the phosphorus burned, the volume of the air at the same time being diminished about one fifth. He observed that a white solid was formed when the phosphorus burned and proved this to be an oxide of phosphorus. These experiments were all carried out with an exactness remarkable for that period.

### OZONE

**Historical.** In 1785 the Dutch chemist Van Marum observed that oxygen through which electric sparks have been passed acquires a peculiar odor. No further attention was given to the observation until 1840, when Schönbein showed that the odor observed by Van Marum was due to the presence of a new gaseous substance formed from oxygen by the action of the electric discharge. Schönbein called the new substance *ozone*, the name being derived from a Greek word signifying "to smell." Finally, in 1856, Andrews proved that ozone is elementary in character, since no material substance is added to oxygen in its conversion into ozone.

**Preparation.** The method used in preparing ozone is the same in principle as that which led to the discovery of the substance, and consists in subjecting oxygen or air to the influence of an electric discharge. It has been found that the yield of ozone can be greatly increased by using the silent electric discharge rather than electric sparks, since in this way it is possible not only to bring a larger volume of oxygen under the influence of the discharge but to do this without raising the temperature to any marked degree and thus to avoid decomposition of the ozone by the heat. An apparatus used for preparing ozone by this method is termed an *ozonizer*.

**An ozonizer.** Fig. 13 represents a common form of ozonizer. Oxygen or air enters at *A* and follows the course indicated by the arrows. The conducting surfaces *B* and *C* are separated by a glass dielectric *D*. Wires leading from an induction coil are connected with *B* and *C*. As the oxygen passes upward between the conducting surfaces it is subjected to the influence of the electric discharge, and a portion of the element is thereby changed into ozone.

To obtain the greatest yield, the oxygen should be cold and free from moisture. Under ordinary conditions not more than

5 per cent of the oxygen is converted into ozone. At lower temperatures a larger yield may be obtained, reaching 90 per cent at the temperature of liquid air. To prepare pure ozone the mixture of oxygen and ozone is cooled with liquid air. The ozone, being much more readily condensed than oxygen, is thereby obtained in a liquid state almost free from oxygen. By evaporating this liquid and again condensing the gas the oxygen present is gradually separated and nearly pure ozone thus obtained.

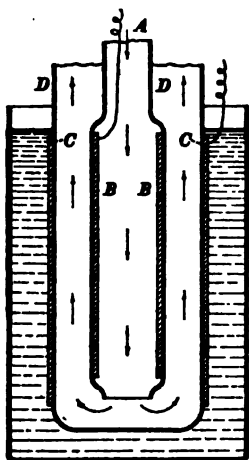


FIG. 13

Ozone is also formed in reactions in which oxygen is liberated at low temperatures, as in the decomposition of water

by the electric current. It is also produced in some oxidations, as when moist phosphorus slowly oxidizes in air.

Its formation by the oxidation of phosphorus may be shown by partially covering with water a few pieces of stick phosphorus placed in the bottom of a jar (Fig. 14). The presence of ozone in the air in the jar is soon indicated by its characteristic odor, as well as by the property it possesses of imparting a blue color to strips of paper (*A*) previously dipped into a solution of potassium iodide and starch. The ozone acts upon the potassium iodide, liberating the iodine present, which in turn forms with the starch a blue substance.

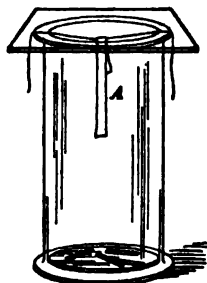
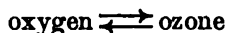


FIG. 14

*It is of much importance to note that the transformation of oxygen into ozone is accompanied by a change in volume, 3 volumes of oxygen forming 2 volumes of ozone.*

The preparation of ozone from oxygen is a reversible change. That only a relatively small percentage of the oxygen subjected

to an electric discharge is transformed into ozone is due to the fact that under all ordinary conditions ozone changes back into oxygen. These two opposite changes may be represented as follows, the arrows indicating the direction in which each change proceeds:



When the speed with which the oxygen changes into ozone exactly equals the speed with which the resulting ozone changes back into oxygen, the two changes are said to be in a state of equilibrium. It is evident that the percentage of ozone present when equilibrium is reached represents the maximum yield under the conditions of the experiment. Such reactions as the above are termed *reversible reactions*.

**Properties and conduct.** Ozone is a gas of pale blue color and characteristic odor. It is 1.5 times as heavy as oxygen, 1 l. of the gas weighing 2.144 g. When cooled sufficiently it condenses to a deep blue liquid which boils at  $-119^{\circ}$  and is, like liquid oxygen, strongly magnetic. Ozone resembles oxygen in its chemical conduct, but is much more active and is therefore a very powerful oxidizing agent. Such metals as silver and mercury, which are not easily acted upon by oxygen, quickly tarnish in air containing ozone. It likewise oxidizes many organic dyes into colorless compounds, acting as a bleaching agent. When pure it is a dangerous explosive, owing to its spontaneous conversion into oxygen, in which change 675 cal. of heat are liberated for each gram of ozone converted.

In view of its great activity it is doubtful whether ozone is ever present in the air in appreciable quantities. It is doubtless formed in a number of natural processes, as by lightning discharge, but it must very speedily disappear through chemical action upon oxidizable materials which are always present.

**Uses of ozone.** Ozone finds increasing commercial applications, all based on its strong oxidizing properties. Thus it is used as a bleaching agent, as a disinfectant, as a deodorizer, and as an oxidizing agent in the preparation of a number of useful

products. It is also being used, especially in Europe, for the sterilization of drinking waters. For these various uses the pure substance is not employed, but ozonized air which is prepared as it is needed.

**The difference between oxygen and ozone.** Experiment has shown that it is possible to change pure oxygen into ozone or ozone into oxygen without change in weight, so that the difference between these two distinct substances cannot lie in the material of which they are composed. The reason for their difference must therefore be sought in the energy relations which exist between them.

In the transformation of oxygen into ozone by the usual method electrical energy is used up, and this must be accounted for, since it cannot be lost. When ozone spontaneously changes into oxygen, 675 cal. of heat are liberated for each gram so changed, and when it acts as an oxidizing agent, the heat evolved is correspondingly greater than when the same oxidation is accomplished by oxygen. Mechanical work also is concerned in the transformation, for there is a change in the volume and a corresponding one in the density of the gas. The simplest way in which to regard these relations is to assume that in the transformation of oxygen into ozone the electrical and mechanical energy absorbed is stored up as chemical energy in the ozone. When ozone spontaneously decomposes or acts upon other substances, this excess energy reappears as heat. Likewise, when ozone is formed by chemical reactions, a part of the chemical energy of the reacting substances is transferred to the ozone.

**Allotropic forms.** We shall find that many of the elements exist in two or more different forms analogous to oxygen and ozone, and that many compounds as well show this peculiarity. Such substances are said to exist in two (or more) *allotropic forms*, and we assume that in each case two allotropic forms possess different energy.

## QUESTIONS

1. What substances mentioned in this chapter are elements and what are compounds?
2. What is the source of the heat evolved in exothermic reactions?
3. Give examples of exothermic and endothermic reactions other than those mentioned above.
4. Why do certain substances, such as sulfur, leave no ash on burning while others, such as iron, leave a solid residue?
5. (a) Why do various kinds of coal (chiefly carbon) differ in the amounts of ash formed on burning? (b) Which kind would you expect to liberate the most heat?
6. What is the common method for removing carbon from the cylinders of gas engines?
7. Flour mills have been known to explode with great violence. Suggest the cause of the explosion.
8. Why do some metals tarnish in air, while others do not?
9. How may the speed of oxidation be increased in the starting of a fire?
10. Why blow a candle to extinguish the flame, but blow a feebly burning fire to make it burn better?

PROBLEMS<sup>1</sup>

1. What is the weight of 100 l. of oxygen?
2. What weight of potassium chlorate will be required for the preparation of oxygen sufficient to fill a gas tank holding 200 l.?
3. Calculate the relative weights of water and mercuric oxide, respectively, that are necessary for the preparation of 200 l. of oxygen.
4. Suppose that 100 g. of potassium chlorate is heated and the oxygen so obtained is used in burning iron. (a) What weight of iron would be burned and (b) what weight of oxide formed?

<sup>1</sup> The data necessary for solving the problems will be found in the preceding chapter. All volumes of oxygen are supposed to be measured at a temperature of 0° C. and under a pressure equal to the normal barometric pressure at the sea level, namely, 760 mm. Consult the table in the Appendix for weights of 1 l. of various gases measured under these conditions.

5. Calculate the relative amounts of heat evolved in the combustion of 100 g. each of carbon and sulfur.

6. Upon the assumption that all the heat could be used effectively, what weight of carbon would have to be burned to furnish sufficient heat to decompose 100 g. of mercuric oxide?

7. What is the difference in energy content (calculated in calories) between 10 g. of oxygen and 10 g. of ozone?

8. In the conversion of 10 l. of ozone into oxygen (a) what volume of oxygen would be formed and (b) what amount of heat evolved?

## CHAPTER III

### HYDROGEN

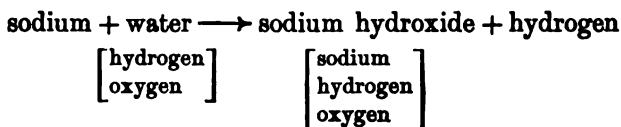
**Historical.** So far as is known, hydrogen was first prepared by Paracelsus (1493-1541), but the English investigator Cavendish is usually regarded as its discoverer, since he was the first to obtain it in pure condition and to recognize it as an independent substance different from other known inflammable gases. This was in 1766. Cavendish termed the gas *inflammable air*, but later, when it was found that it was a constituent of water, Lavoisier renamed it *hydrogen*, signifying "water former."

**Occurrence.** In the free condition hydrogen is sometimes found in gases issuing from the earth in volcanic regions. It has also been found in the atmosphere, but only in very minute quantities. The spectroscope reveals large quantities of the free element in the gases surrounding the sun and certain other stars. Combined with oxygen in the form of water it is widely distributed. Combined with carbon it forms a large number of compounds known as *hydrocarbons*, which constitute by far the greater part of ordinary natural gas and petroleum. It is likewise a constituent of the compounds present in living organisms and of most of the products derived from them, such as sugar, starch, and butter.

**Preparation of hydrogen.** Since hydrogen is not found in the free condition to any extent, it must be prepared by liberating it from its compounds. The compounds most often used as sources of hydrogen are (1) water, (2) acids, and (3) bases.

1. **Preparation from water.** Hydrogen may be liberated from water by two general methods: (a) by the action of the electric current, as described under the methods for the preparation of oxygen (p. 20); (b) by the action of certain metals. A few

metals, such as sodium, potassium, and calcium, act rapidly upon water even at ordinary temperatures, liberating one half of the hydrogen present in the water. The remainder of the hydrogen, together with all the oxygen, combines with the metal to form compounds known as hydroxides. The reaction which takes place when water is decomposed by sodium may be represented as follows:



**Apparatus.** Fig. 15 represents a form of apparatus used in preparing hydrogen by this method. A pellet of sodium is pushed into the end of a short piece of lead or tin pipe, the other end of the pipe being hammered until closed. The pipe containing the sodium is then dropped into a trough of water arranged as shown in the figure. The hydrogen liberated by the action of the sodium upon the water rises in bubbles and is caught in the jar. The sodium hydroxide formed in the reaction may be recovered as a white solid by evaporating the water remaining after the action is completed.

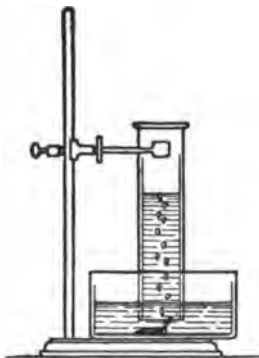
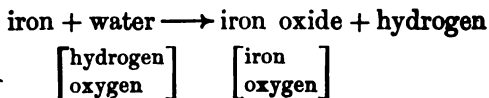


FIG. 15

Other metals, such as magnesium and iron, also decompose water rapidly, but only at high temperatures. In such cases the decomposition is best effected by heating the metal to redness in an iron or porcelain tube and then passing steam over the red-hot metal. Under these conditions the metal combines with the oxygen of the water to form an oxide, while the hydrogen is liberated. For example, in the case of iron the reaction may be represented as follows:



**Apparatus.** Fig. 16 represents a simple form of apparatus which may be used in preparing hydrogen by this method. Iron in the form of fine wire or tacks is placed in the tube *A* and heated to a high temperature. The water in flask *B* is then boiled and the resulting steam passed into *A*. The iron in the tube combines with the oxygen of the steam to form oxide of iron, which, being a solid substance, remains in the tube, while the hydrogen passes on and is collected in the receiver *C*, as is shown in the diagram.

2. *Preparation from acids.* The term *acid* is applied to an important class of compounds, whose characteristics will be discussed fully in a later chapter; for the present it will suffice

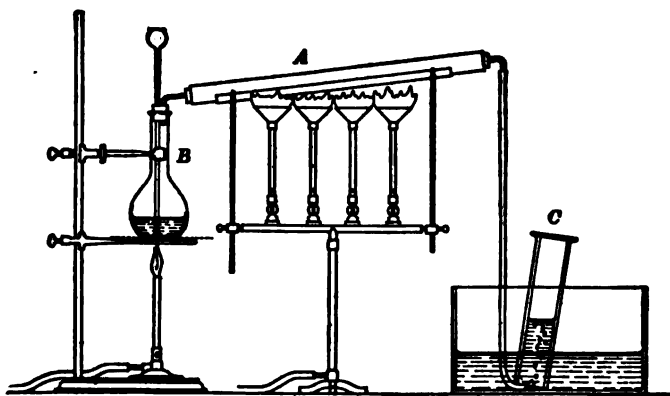


FIG. 16

to say that all acids contain hydrogen and that this hydrogen is liberated when the acid is brought in contact with certain metals. This reaction furnishes a convenient method for preparing hydrogen in the laboratory. For this purpose any of the metals which liberate hydrogen from water, but only these, may be employed. Usually zinc or iron is used. The acids commonly employed are either hydrochloric acid or sulfuric acid. The former is a compound containing 2.76 per cent of hydrogen and 97.24 per cent of chlorine, while the latter is a compound containing 2.06 per cent of hydrogen, 32.69 per cent of sulfur, and 65.25 per cent of oxygen. To liberate hydrogen

it is only necessary to bring the acid, properly diluted with water, into contact with the metal. The metal gradually passes into solution, while the hydrogen of the acid is in turn set free. The liberation of the hydrogen is indicated by the effervescence of the liquid. When zinc and sulfuric acid are used in the preparation, the reaction may be represented in a general way as follows:

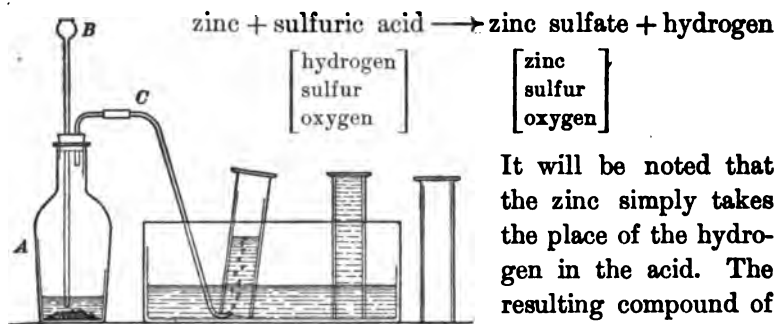
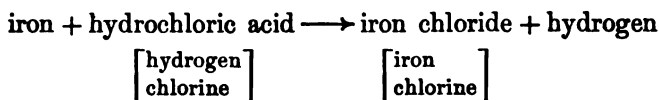


FIG. 17

It will be noted that the zinc simply takes the place of the hydrogen in the acid. The resulting compound of zinc, sulfur, and oxygen, known as zinc

sulfate, is a white solid which remains dissolved in the water present and may be obtained by evaporating the solution.

When iron and hydrochloric acid are used in the preparation of hydrogen, the reaction may be represented as follows:



**Apparatus.** A convenient form of apparatus for preparing hydrogen by the action of metals upon acids is shown in Fig. 17. The metal is placed in flask A, which is fitted with a cork and connected with tubes, as shown in the figure. The acid, properly diluted with water, is added a little at a time through the funnel tube B. The liberated hydrogen escapes through C and is collected in receivers, as shown in the figure. The hydrogen which first escapes through the exit tube is mixed with the air originally present in flask A. *Such a mixture of hydrogen and air is violently explosive when brought in contact with a flame.* Therefore one must keep all flames away from the apparatus. Moreover, one should not collect the hydrogen

until an amount of it has been generated sufficient to displace all the air previously contained in the flask and in the delivery tube *C*.

A more convenient form of apparatus to use is that shown in Fig. 18. It is known as a Kipp generator and has the advantage of being automatic in its action. The metal is placed in *A*, and the acid poured into *B*. When the stopcock *D* is opened, the acid runs down into *C* and up into *A*, where it comes in contact with the metal. The hydrogen generated escapes through *D*. If now the stopcock is closed, the hydrogen, being unable to escape through the tube, pushes the acid away from the metal in *A* down into *C* and up into *B*, so that the action ceases until the stopcock is again opened.

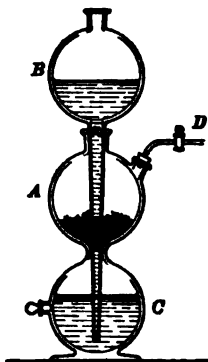
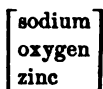
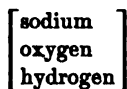


FIG. 18

3. *Preparation from bases.* The bases are compounds of a metal with oxygen and hydrogen. Certain metals, such as zinc and aluminium, react with some of the bases, especially sodium hydroxide, liberating the hydrogen present in them. Thus, when zinc is added to a solution of sodium hydroxide and the mixture is heated, the zinc takes the place of the hydrogen of the base. The reaction may be represented as follows:

zinc + sodium hydroxide  $\longrightarrow$  sodium zincate + hydrogen



**Commercial method of preparation.** When wanted in large quantities hydrogen is prepared by the action of steam or sulphuric acid upon iron, or by the decomposition of water by the electric current. It is also prepared economically by liberating it from water through the action of carbon, by dissolving the element silicon in a solution of sodium hydroxide, and by the decomposition of the compound of hydrogen and carbon known as acetylene. These methods will be discussed in later chapters.

**Properties.** Hydrogen, like oxygen, is a colorless, odorless, and tasteless gas. It has the greatest specific heat, as well as

the highest thermal conductivity, of any gas. One liter of it weighs 0.08987 g. It is the lightest of all known substances, being 14.385 times lighter than air; it may therefore be transferred from one vessel to another by pouring it *upward*, as shown in Fig. 19. The hydrogen in the cylinder *A* rises to the top of the cylinder *B* and forces the air out. The solubility of hydrogen in water is very small, being only about one half as great as that of oxygen.

Dewar was the first to obtain hydrogen in the liquid state. He cooled the gas to a very low temperature by means of liquid air, and at the same time subjected it to a pressure of 180

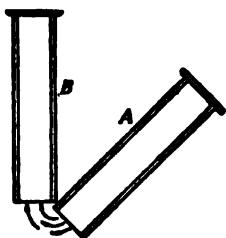


FIG. 19

atmospheres. In this way it was obtained as a colorless, transparent liquid, boiling at  $-252.7^{\circ}$  under a pressure of 1 atmosphere. This is the lightest liquid known, having a density of but 0.07 at its boiling point. When liquid hydrogen is evaporated under very small pressure, solid hydrogen is obtained as a transparent, snowlike body melting at  $-259^{\circ}$ .

A large number of metals have the property of absorbing or *occluding* hydrogen. The quantity so absorbed by most of the metals is not large, but a few, such as gold, platinum, and especially palladium, take up large volumes of the gas. The quantity absorbed varies not only with the metal but also with the physical condition of the metal, as well as with the temperature and pressure under which the absorption takes place. One volume of palladium, in the form of a powder, at ordinary temperatures absorbs over 800 volumes of the gas. It is because of this property that hydrogen, when conducted into hot tubes made of iron or platinum, passes through the walls of the tube to a considerable extent.

The absorption of hydrogen by palladium can be strikingly shown by using strips of this metal as electrodes in the decomposition of water by the electric current. When the circuit is closed, oxygen is at once evolved at

one electrode and hydrogen at the other. It will be noted, however, that the amount of hydrogen evolved at first is relatively small, but gradually increases as the palladium becomes saturated with the gas.

**Chemical conduct.** Although hydrogen is inactive at ordinary temperatures, nevertheless under proper conditions it combines directly with many of the elements and even decomposes some compounds by uniting with certain elements present in them. Just as the compounds of oxygen with any other one element are termed *oxides*, so those containing hydrogen in combination

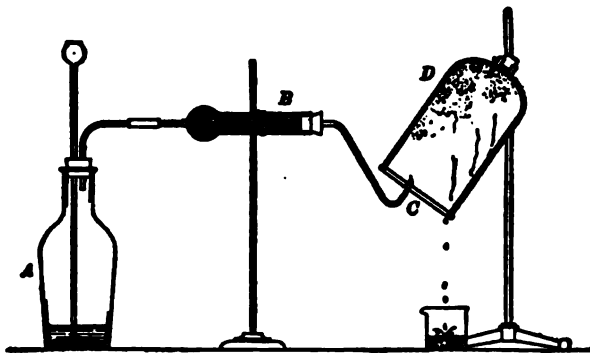


FIG. 20

with another element are, as a class, known as *hydrides*. Many of the individual members of this class of compounds, however, have other names.

1. *Action of hydrogen upon elements.* At suitable temperatures hydrogen combines directly with nitrogen to form the gaseous compound known as ammonia, with sulfur to form the foul-smelling gas known as hydrogen sulfide, with chlorine to form hydrogen chloride, more often called hydrochloric acid. The union with chlorine can also be brought about by strong light, a mixture of hydrogen and chlorine exploding with great violence when exposed to direct sunlight. Hydrogen also combines with a number of the metals. It is characterized especially, however, by its affinity for oxygen, with which it combines to

form water. *Experiments show that the ratio in which these two gases combine is 1 of hydrogen to 7.94 of oxygen by weight, or 2.0024 of hydrogen to 1 of oxygen by volume.* A large amount of heat is set free in this reaction. For each gram of hydrogen entering into combination with the oxygen there is liberated 28,933 cal. if the water produced remains in a state of vapor, or 34,221 cal. if the resulting vapor is condensed to liquid form.

The union of hydrogen and oxygen, and the resulting formation of water, is best shown by burning hydrogen in oxygen or air. A convenient apparatus is shown in Fig. 20.

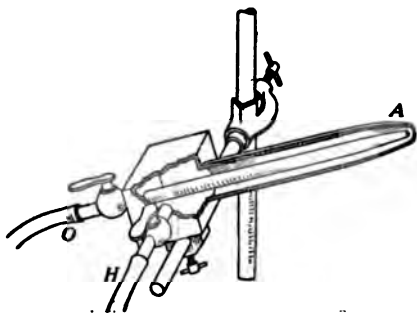


FIG. 21

The hydrogen is generated in flask *A* and passed through the tube *B* filled with porous calcium chloride, which removes the moisture from the gas. After the air has been displaced from the apparatus, the hydrogen escaping at the jet *C* is ignited. Almost instantly a dewlike substance is deposited on the cold sides of the jar *D*. This may be collected and proved to be water.

The hydrogen, if pure, burns with a colorless but very hot flame. When burned in air much of the heat resulting from the union of the hydrogen and oxygen is absorbed in heating the inert nitrogen present. To obtain the maximum temperature one must use pure oxygen instead of air. Moreover, the hydrogen and oxygen must be brought together in the proportion in which they unite; otherwise the gas which is left uncombined will absorb a portion of the heat. An apparatus arranged for burning hydrogen in this way is known as the *oxyhydrogen blowpipe*. This consists primarily of two tubes (Fig. 21), one inside the other. Hydrogen is forced in through the tube *H* and ignited at the end of tube *A*. Oxygen is then forced in through the tube *O*. The two gases are thus brought together at the tip

of the tube *A*, and combine with the evolution of a large amount of heat. Under most favorable conditions a temperature of about  $2500^{\circ}$  may thus be obtained. Ordinarily, however, the temperature reached does not exceed  $1800^{\circ}$ . At the high temperature of the flame a piece of lime glows intensely, while an iron wire burns with the greatest brilliancy. Platinum (melting point  $1755^{\circ}$ ) is readily melted when exposed to it.

While it is thus possible to burn hydrogen safely in air or pure oxygen by limiting the amounts of the two gases brought in contact with each other at any instant, mixtures of the gases in any considerable quantities explode with terrific violence when ignited.

#### **Explosion of a mixture of hydrogen and oxygen.**

A bell jar having a capacity of two or three liters is fitted with a cork provided with a short open tube of about 1 cm. diameter, as shown in Fig. 22. The tube is closed with a small rubber stopper, and the bell jar filled with hydrogen, the gas being collected over water. When entirely filled the jar is set on blocks of wood, the stopper removed, and the hydrogen ignited at the top of the tube. As the hydrogen rises through the tube and is burned, air enters the jar from below and mixes with the remaining hydrogen. When a volume sufficient to form an explosive mixture with the hydrogen has thus entered the jar, a violent explosion results. Since the jar is open at the bottom, and the intensity of the explosion is diminished by the presence of the nitrogen in the air, there is no danger attending the experiment. The explosion of the two gases reaches the maximum effect with mixtures of pure hydrogen and oxygen in the exact proportion in which they combine. Such mixtures should never be exploded except in small quantities and by experienced chemists.

**Speed of combustion of hydrogen with oxygen.** The union of hydrogen and oxygen probably takes place at ordinary temperatures, but the speed of the reaction is so slow that no change can be detected even after long intervals of time (p. 33). As the temperature is raised the speed increases. Thus Meyer and Raum found that the two gases, when mixed in the proportion of two volumes of hydrogen to one volume of oxygen and heated to  $100^{\circ}$  for 218 days showed no appreciable combination. When heated to  $300^{\circ}$  for 65 days it was found that, in different trials, from 0.4 per cent to 9.5 per cent of the mixture had combined. At  $500^{\circ}$  the change is still more marked, but takes place gradually and requires several

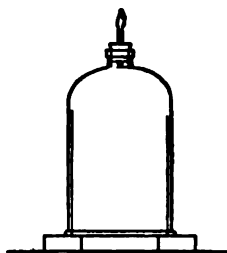


FIG. 22

hours for completion. At a temperature roughly approximating  $800^{\circ}$  the union of the two takes place with explosive violence. The temperature at which this instantaneous combination takes place is constant when the conditions are exactly the same. It is modified, however, by very slight changes in these conditions, due to the catalytic effect of foreign substances, such as moisture and the materials of which the tube containing the gases is made. Certain catalyzers, such as finely divided platinum, bring about practically instantaneous combination at ordinary temperatures.

**2. Action of hydrogen upon compounds.** Hydrogen not only combines directly with many elements, such as chlorine and oxygen,

when present in the free state, but under favorable conditions it will remove these elements from some of their compounds.

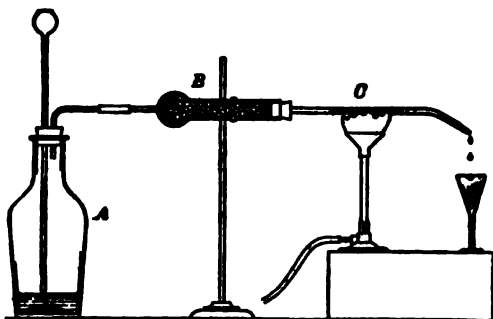
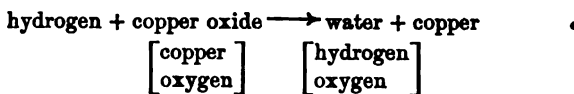


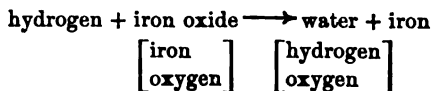
FIG. 23

**Action of hydrogen on copper oxide.** This action may be shown by introducing some black oxide of copper into a hard glass tube *C* (Fig. 23), which is connected with a hy-

drogen generator *A* and drier *B*, as shown in the figure. Hydrogen is generated, and *after the air has been completely displaced from the entire apparatus*, the tube containing the oxide of copper is heated. The hydrogen combines with the oxygen present in the copper oxide to form water, which condenses in the colder portions of the tube near the end, while the black color of the oxide of copper gradually gives way to the reddish tint of copper as the action progresses. The change may be represented as follows:

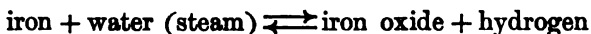


Many other metallic oxides, such as that of iron, may be substituted for the oxide of copper in this experiment. When oxide of iron is used, the change may be represented as follows:



**Reduction ; reducing agent.** When oxygen is removed from a compound, the change is known as *reduction*. The compound from which the oxygen is removed is said to be *reduced*, while the substance which unites with the oxygen is called the *reducing agent*. Thus, in the experiment with the oxide of copper the hydrogen is termed the reducing agent and the copper oxide is said to be reduced. It will be observed that reduction is just the reverse of oxidation. In the latter process oxygen is added to a substance, and in the former it is taken away. The more comprehensive meaning of the terms *oxidation* and *reduction* will be given in a later chapter.

**The reaction between hydrogen and oxide of iron.** It will be observed that the reaction which takes place when hydrogen is passed over heated iron oxide (see above) is just the reverse of that which takes place when steam is passed over red-hot iron (p. 44). In the one case hydrogen and iron oxide react to form water and iron ; in the other the iron and water react to form iron oxide and hydrogen. The two reactions may be expressed as follows :



This reaction is similar to that which takes place in the conversion of oxygen into ozone, and of barium oxide into barium peroxide, in that it is reversible. Under the same set of conditions the two opposing reactions may go on until an equilibrium is reached. It is possible, however, to devise conditions under which one of the reactions is so much aided as to practically reach completion. This subject will be more systematically discussed in Chapter XVIII.

**Physiological action of hydrogen.** Pure hydrogen is not poisonous and may be breathed without danger, but the sulfuric acid and zinc used in its preparation frequently contain small amounts of arsenic, and the hydrogen generated from such substances is mixed with a gaseous compound of arsenic and hydrogen, which is exceedingly poisonous and must not be inhaled.

**Uses of hydrogen.** Formerly considerable quantities of hydrogen were used in the oxyhydrogen blowpipe, but for this purpose it has been displaced almost entirely by the gaseous compound of carbon and hydrogen known as acetylene (see oxyacetylene blowpipe). Hydrogen is employed as a reducing agent, especially in the process of refining certain oils, whereby such oils as cottonseed oil are converted into solid fats suitable for foods. Because of its extreme lightness it is used for inflating dirigible airships and observation balloons, and large amounts were used for this purpose in the World War. Germany used free hydrogen during the war for making ammonia and it is probable that this method will come into general use at no distant date (see commercial production of ammonia).

### QUESTIONS

1. Mention the experiments in which sodium hydroxide was used or formed in connection with the preparation of oxygen and hydrogen.
2. Water dissolves common salt (sodium chloride) and sulfuric acid dissolves zinc. In what respect do the two processes differ from each other?
3. Why is sulfuric acid added to water before decomposing the latter by an electric current?
4. (a) In the oxyhydrogen blowpipe (Fig. 21) why does the inner tube extend to the tip of tube *A*? (b) Why force oxygen through the inner tube rather than the outer?
5. Why not enlarge the inner tube of the oxyhydrogen blowpipe and use air in place of pure oxygen?
6. Contrast hydrogen and oxygen as to (a) weight; (b) boiling point; (c) melting point.
7. If you wish to manufacture hydrogen commercially, what factors would you take into consideration in selecting the method of manufacture?
8. In the apparatus shown in Fig. 17, should the delivery tube *B* dip below the surface of the liquid in the flask *A*, or end above it? Why should the tube *B* in Fig. 8 end above the material in the flask *A*?

## PROBLEMS

1. Suppose you had 1 kg. of water with which to prepare hydrogen. Which of the following methods would yield the largest amount of hydrogen: (a) decomposition by the electric current; (b) decomposition by iron; (c) decomposition by sodium?

2. 1 kg. of water is boiled and the steam passed over hot iron. (a) What is the volume of hydrogen liberated? (b) What is its weight? (c) What is the change in weight which the iron has undergone? (d) How many calories would be evolved in the combustion of the hydrogen formed? (e) What would be the weight of the water formed?

3. In passing hydrogen over heated copper oxide (Fig. 23) 22.5 g. of water was formed. What is the loss in the weight of the copper oxide?

4. Suppose that 10 l. of hydrogen and 15 l. of oxygen were mixed together and ignited. What would be the products of the reaction? Calculate the weight of each.

5. Calculate the volume of hydrogen that could be obtained from each of the following: (a) 100 g. of sulfuric acid; (b) 100 g. of hydrochloric acid; (c) 100 g. of water.

## CHAPTER IV

### PROPERTIES OF GASES

The gaseous state a property of all substances. Experiment has shown that every substance tends to pass into the gaseous state if its temperature is raised sufficiently, but it is not always possible to actually bring about such a change. In some cases the temperature required is so high that it cannot be attained by laboratory methods; in others the substance decomposes before the required temperature is reached. For example, it will be recalled that mercuric oxide and potassium chlorate yield oxygen when heated, while sugar decomposes into carbon, water vapor, and other products.

Experience also shows that at some lower temperature every gas condenses to a liquid or a solid. Earlier in the history of science, when the laws governing gases were not so well known as they are now, some gases, including oxygen, nitrogen, and hydrogen, resisted all efforts directed toward their liquefaction, and these were termed *permanent* gases. All known gases, however, have now been liquefied.

**Characteristics of the gaseous state.** 1. *Expansibility.* The most striking characteristic of a gas is its tendency to expand indefinitely, so as to distribute itself uniformly throughout all the space in which it is confined. If the gas is suddenly set free in a vacuum, this distribution occurs with great rapidity.

**Apparatus.** This rapid distribution of a gas throughout a vacuum may be demonstrated by the following experiment: A small, thin-walled bulb *A* (Fig. 24) is filled with bromine, sealed, and placed in a glass vessel *B*, which can be closed and exhausted by a water pump attached at *C*. A glass rod is arranged to slip through a tight-fitting rubber stopper *D*. When the vessel has been exhausted, the rod is pushed down so as to crush the bulb. Instantly the reddish vapor of bromine fills the vessel.

If the gas is set free in a space already occupied by another gas, the distribution takes place very slowly. The one gas is said to *diffuse* through the other, which presents a certain obstacle to its spread. Sooner or later, however, the two become evenly mixed. The vapor resulting from the evaporation of a few drops of bromine may gradually be perceived by its odor in every part of a large room.

Diffusion will take place quite independently of the relative weights of the two gases. We may introduce a heavy gas under a lighter one in a closed vessel, but diffusion will take place, notwithstanding the difference in density. Likewise two gases of unequal density, when once mixed, show no tendency to separate into layers, with the heavier one below the lighter. Complete and permanent diffusion is characteristic of all gas mixtures.

2. *Compressibility*. A second and equally important characteristic of gases is their compressibility. Liquids and solids are very little affected by pressure, but the volume of a gas is very greatly altered by comparatively small changes in pressure. A very familiar illustration of this is found in the common experience of pumping up a bicycle or automobile tire. A surprising volume of air may be pumped into what is an almost unchanged volume in the tire.

Obviously, before we can get a clear idea as to the density of a gas, that is, *the mass of unit volume*, or *the concentration*, we must have an understanding of the way in which the volume of a given mass changes with the various physical conditions, and we must adopt a set of standard conditions under which all measurements are to be made.

**The gas laws.** A large number of laws relating to gases have been formulated, and many of these will be mentioned in subsequent pages. At present it will be sufficient to consider four,

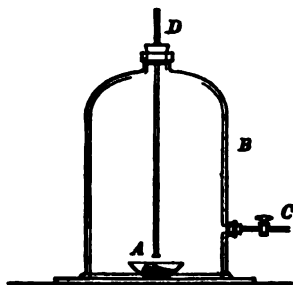


FIG. 24

which will serve to define the conduct of gases under the usual variety of conditions, especially of pressure and temperature.

1. *The relation of volume to pressure; the law of Boyle.* In 1660 Robert Boyle, an Englishman of remarkable scientific accuracy for his time, made some careful measurements upon the compressibility of gases. He succeeded in establishing the generalization known as *Boyle's law*, which may be stated thus: *The volume which a given mass of a gaseous substance occupies is inversely proportional to the pressure under which it is measured, provided the temperature remains constant.* Doubling the pressure diminishes the volume one half; diminishing the pressure one half doubles the volume. The product of the pressure into the volume is therefore constant. Stated in algebraic form, we have the equation

$$P_1 V_1 = P_2 V_2 = C \quad (1)$$

in which  $P_1$  and  $V_1$  are the pressure and volume of a given mass of gas under one set of conditions, and  $P_2$  and  $V_2$  those under another,  $C$  being their constant product. The magnitude of  $C$  will of course depend upon the quantity of gas taken for experimentation.

Like most of the laws of science, Boyle's law is only an approximate statement of the facts, since all gases do not act in precisely the same way, and extreme conditions introduce irregularities. For example, hydrogen gas is not as compressible as the law leads us to expect; at very high pressures all gases resist pressure more than at moderate pressures; when increase of pressure brings the gas near its point of liquefaction, it is more easily compressed than the law predicts. Within the range of accuracy required for most chemical purposes, however, Boyle's law is a remarkably exact statement of the facts and holds true for all gases.

**Illustration of the law of Boyle.** A typical example will make the meaning of this law clear. Suppose that a gas, measured under a pressure of 720 mm., has a volume of 620 cc. What volume will this gas occupy under standard pressure (760 mm.), the temperature remaining constant?

According to Boyle's law,  $P_1 V_1 = P_2 V_2$ . Substituting the values given in the problem, we have  $760 \times V_1 = 720 \times 620$ ; or  $V_1 = 587.4$  cc.

**Standard pressure.** For practical purposes we must choose some standard pressure to which all gas volumes are to be referred. This is most conveniently chosen as the average pressure of the atmosphere at the sea level. This is equal to the pressure exerted by a column of mercury 760 mm. in height, or to 1088 g. per square centimeter.

**The graphic representation of Boyle's law.** Relations like those stated in Boyle's law are best represented by a curved line every point on which

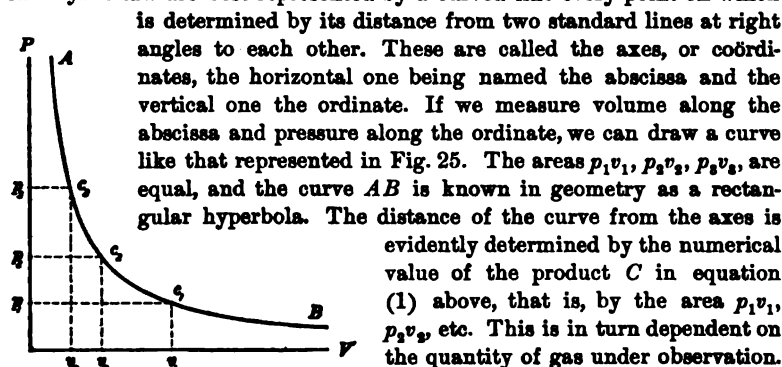


FIG. 25

## 2. The relation of volume to temperature; the law of Gay-Lussac (or

*of Charles*). Experiments show that all gases expand when the temperature is raised (the pressure being held constant), and that equal volumes of all gases expand to the same extent for a given increase in temperature. Let us suppose that the volume of the gas has been measured at zero on the centigrade scale. Experiment shows that a rise of one degree causes an expansion equal to  $\frac{1}{273}$  of this volume; a rise of two degrees, an expansion of  $\frac{2}{273}$ . That is to say, if 273 cc. of the gas is measured at zero, the volume at  $1^\circ$  above will be 274 cc.; at  $2^\circ$  above, 275 cc. At  $1^\circ$  below it will contract to 272 cc., and at  $2^\circ$  below, to 271 cc. If the same rate of contraction holds good at all temperatures, then at  $-272^\circ$  the volume will be

1 cc., and at  $-273^{\circ}$  the volume will be zero. Obviously this last conclusion cannot be true, but it must mean that before such a temperature is reached, all gases will have become liquids, in which state the law will not apply. This interpretation is borne out by the fact that helium, the most difficult of all gases to liquefy, passes into a liquid at  $-268.7^{\circ}$ .

If we were to construct a thermometer having divisions of the same size as those on the centigrade scale, but with the zero point at  $-273^{\circ}$  on the latter scale, then the point at which water freezes would be  $273^{\circ}$ . At  $272^{\circ}$  on this scale the 273 cc. of gas discussed in the last paragraph would measure 272 cc.; at  $271^{\circ}$ , 271 cc.; at  $1^{\circ}$ , 1 cc. On such a scale the volume of the gas would be proportional to the temperature at every point. This is known as the scale of *absolute temperatures, the point  $-273^{\circ}$  on the centigrade scale being absolute zero*. Evidently the absolute temperature may be obtained by adding  $273^{\circ}$  to the centigrade reading.

The law established by Gay-Lussac may now be stated in the following quantitative form: *The volume occupied by a given mass of a gas at different temperatures is proportional to the absolute temperature (pressure remaining constant)*. If  $V_1$  and  $V_2$  are the volumes at the absolute temperatures  $T_1$  and  $T_2$ , then

$$\frac{V_1}{V_2} = \frac{T_1}{T_2}, \text{ or } V_1 = \frac{V_2 T_1}{T_2} \quad (2)$$

**Illustration of the law of Gay-Lussac.** The following example will make the meaning of the law clear. The volume of a certain gas measured at a temperature of  $70^{\circ}$  is 650 cc. What will be its volume at  $10^{\circ}$ ?

First reduce the centigrade readings to absolute:

$$70^{\circ} \text{ C.} = 70 + 273 = 343^{\circ} \text{ A.}; \quad 10^{\circ} \text{ C.} = 10 + 273 = 283^{\circ} \text{ A.}$$

Now substituting the appropriate values in the above equation, we have

$$\frac{V_1}{650} = \frac{283}{343}; \text{ or } V_1 = 536.3 \text{ cc.}$$

*Variations in volume due to changes in both pressure and temperature.* In case both pressure and temperature change, then the

correction may be made for each in succession. It is more convenient, however, to combine equations (1) and (2), which express respectively Boyle's law and Gay-Lussac's law, and use this new equation for the solution of such problems. This new equation is

$$V_1 = \frac{P_2 V_2 T_1}{P_1 T_2} \quad (3)$$

The following example will illustrate the use of this equation : A gas measured 1000 cc. at a temperature of 50° and under a pressure of 740 mm. What volume will it occupy at a temperature of 27° and under a pressure of 760 mm. ? By substituting the proper values in equation (3) we have

$$V_1 = \frac{740 \times 1000 \times 300}{760 \times 323} = 904.3 \text{ cc.}$$

*Standard conditions.* To the standard pressure already adopted we must now add a standard temperature, and this is chosen as 0° centigrade (equal to 273° absolute). These two conditions of temperature and pressure are known as the *standard conditions*. Whenever the volume of a gas is given, say 100 l. of oxygen, it is understood, unless otherwise specified, that the gas occupies this volume when measured at a temperature of 0° and when subjected to a barometric pressure of 760 mm.; or in other words, when measured under standard conditions. Moreover the statement that 1 l. of oxygen weighs 1.429 g. means that 1 l. of the gas measured under standard conditions weighs 1.429 g.

Now suppose we designate the volume occupied by a definite weight of gas when measured under standard conditions by  $V_s$ ; then  $V_s$ , 760, and 273 will be the values of volume, pressure, and temperature under one standard set of conditions and will correspond to one set of values in equation (3). Substituting them in place of  $V_1$ ,  $P_1$ ,  $T_1$ , and dropping the subscript of the values  $V_s$ ,  $P_s$ ,  $T_s$  as no longer necessary, we get the equation

$$V_s = \frac{P \times V \times 273}{760 \times T} \quad (4)$$

Thus, suppose we have prepared oxygen in the laboratory and find that the gas measures 685 cc. under the laboratory conditions, namely,  $22^{\circ}$  and 750 mm., and we wish to know what volume this gas would measure under standard conditions. By substituting the proper values in equation (4) we get:

$$V_s = \frac{750 \times 685 \times 273}{760 \times (273 + 22)} = 625.57 \text{ cc.}$$

3. *The relation of temperature to pressure.* We have seen that when the pressure is maintained constant, the volume increases in proportion to the absolute temperature. From this, together with Boyle's law, it follows that if the volume is kept constant, the pressure will increase in proportion to the absolute temperature. Gay-Lussac made some experiments upon this point and found that the pressure does so increase. This principle is not of as frequent application in chemical calculations as the more familiar law of Gay-Lussac, but in many lines of mechanics it is of importance. For example, it enables us to calculate the pressure in a steam boiler at a temperature  $t$ , if we know the value at some other temperature  $t'$ . By measurement of the pressure reached in an explosion we may also calculate the temperature, or vice versa.

4. *The rate of diffusion; the law of Graham.* In 1833 the Scottish chemist Thomas Graham made a series of studies upon what he called the rate of *diffusion* of gases, by which he meant the rate at which various gases will pass through a minute pinhole, or through porous materials such as unglazed pottery. As a result of his experiments he found that under definite conditions of temperature and pressure *the rate of diffusion is inversely proportional to the square root of the density of the gas.* Of two gases the lighter will therefore diffuse the more rapidly. Oxygen and hydrogen have densities which are almost exactly in the ratio 16:1, and their rates of diffusion are therefore in the ratio

$$\frac{1}{\sqrt{16}} : \frac{1}{\sqrt{1}} = \frac{1}{4} : \frac{1}{1} = 1 : 4$$

In other words, hydrogen will leak through fine pores four times as fast as oxygen.

**Demonstration of diffusion.** This property may be demonstrated by the use of the apparatus represented in Fig. 26. A small battery jar *A* is connected with a tight-fitting rubber stopper or plaster-of-Paris joint with a glass tube *B*, the other end of which passes just through a stopper in the vessel *C*. The vessel is half filled with water and is provided with a second tube *D*, drawn to a small jet at *E* and extending to the bottom of the vessel *C*. A bell jar or large beaker *F* is supported over the battery jar, and under its edge extends the end of a tube *G* connected with a source of hydrogen. When hydrogen is admitted to the space under the cover *F*, it passes into the porous jar faster than the air within passes out, developing a pressure within the jar. This is communicated to the surface of the water in *C*, forcing some of it out through the jet *E* as a fountain.

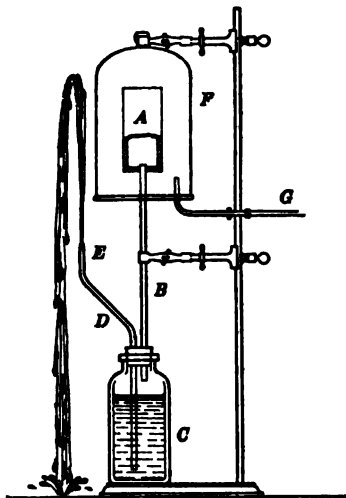


FIG. 26

**The meaning of laws in science.**

The four laws just considered are merely general statements in regard to the conduct of gases as determined by experiment. Like

all other scientific laws, they offer no explanation of the facts which they state, nor do they place any restriction upon nature which compels obedience, as the laws enacted by a legislature bind society. They are simply concise statements of what might be called the *habits of nature* as observed in experiment.

**Forming a theory.** It is certainly a very striking fact that all gaseous substances behave in so simple a manner, quite irrespective of their chemical nature. It would appear most probable that this must be due to some very simple mechanical structure which gases have in common, and the mind at once begins to imagine a mechanical model which, if real, would act in the same manner. *The process of constructing a mental picture of this*

*kind is called forming a theory.* The theory which has proved to be the most satisfactory in connection with the properties of gases is known as the *kinetic theory of gases*. It will be instructive to follow it out to some extent, as it will show very clearly how a theory is developed, and it will be found very useful in subsequent pages.

**The chief points in the kinetic theory.** A number of points may be presented which must be taken into account in any theory that may be framed in regard to the nature of gases:

1. All gases appear to have the same mechanical structure, since they respond in the same way to energy changes such as those of temperature and pressure.

2. They cannot be in any sense continuous matter, but must be extremely porous, since they are always very compressible and also tend to expand indefinitely.

3. The pressure which gases exert cannot be the thrust of a rigid body, as of a spring, and, under the circumstances, almost the only other way in which we can imagine the application of a pressure is by the momentum of moving bodies. Hence we may imagine a gas to be made up of moving particles whose aggregate impact is the cause of the pressure exerted upon the walls of a containing vessel.

4. Boyle's law states that when the volume is reduced one half, the pressure exerted by the gas is doubled. This is in accord with the picture that we are drawing, for in the half volume the particles will strike the walls of the vessel twice as often, and will therefore exert twice the force on the same area in a given time.

5. Since rise of temperature increases the pressure, it must in some way increase the kinetic energy of the moving particles. This might be brought about by increasing either the mass or the speed of the particles, for their kinetic energy is equal to the expression  $\frac{1}{2} ms^2$ , in which  $m$  represents the mass and  $s$  the speed. Experiment shows that the mass of a gas is not changed by heat; so it must be the speed of the particles which is affected.

6. The pressure of all gases increases equally for equal rise in temperature ; so the aggregate energy of the various kinds of gas particles must increase to the same degree. Now it can be shown that the masses of two kinds of gas particles are different ; therefore the speed of the particles must be increased inversely as the square root of their mass, in order that the value  $\frac{1}{2} ms^2$  may be equally increased for two different particles.

7. All the facts of diffusion are in accord with the idea that gases are made up of moving particles, and Graham's law, which states that the rate of diffusion is inversely proportional to the square root of the density of a gas, is but another way of stating the conclusions of the preceding paragraph.

8. Finally, our picture becomes clearer and more harmonious if we assume that in equal volumes of all gases there is the same number of particles or *molecules*, as they are called. This assumption is known as *Avogadro's hypothesis*. It may be deduced mathematically from the quantitative laws we have had before us, and it is in accord with many chemical facts to be discussed later on.

**Summary of the kinetic theory.** As a picture which gives a graphic representation of the simple conduct of gases, the kinetic theory suggests (1) that all gases are made up of small particles called molecules, relatively far apart and in violent motion, (2) that equal volumes of all gases under the same conditions of temperature and pressure contain the same number of molecules, whose momentum is the cause of pressure, and (3) that the kinetic energy of all molecules is increased equally by a given rise in temperature, the increase being due to the increased speed of the particles.

**Value of a theory.** The value of such a theory is at once apparent. It presents a mental picture which assists the memory in retaining a great variety of facts. It suggests many experiments which otherwise might never be undertaken, for our first impulse, after forming such a theory, is to test it experimentally in every possible way. It enables us to form a probable opinion in cases where experiment has not yet made a definite decision.

It leads to the correction of errors that have crept into the body of our knowledge as a result of faulty experiments.

There is, however, a real peril in accepting a theory. The whole picture may be wrong, yet it may seem so plausible that we rest contented with it and fail to see its faults. Its very plausibility may prevent us from making experiments which would disclose the error in the theory and put us on the right track.

**Final outcome of a theory.** It may happen that increasing knowledge will demonstrate beyond any possible doubt that a given theory is a correct representation of things as they really are. The theory, relieved of every element of uncertainty, then becomes a *truth*. For example, no one any longer questions the truth of the kinetic theory of gases.

On the other hand, so many things may be found that are incompatible with the theory that it becomes clear that the whole picture it presents is inadequate and cannot represent the truth. As soon as we are able we devise a more satisfactory theory, and having done so, we abandon the earlier one. This was the history of the phlogiston theory of combustion that was replaced by the oxygen theory, now become a truth.

### QUESTIONS

1. What conditions determine whether a substance such as hydrogen or oxygen or water assumes the gaseous, liquid, or solid state?
2. Mention some discovery made by each of the following chemists: (a) Priestley, (b) Cavendish, (c) Scheele, (d) Gay-Lussac, (e) Boyle, (f) Lavoisier, (g) Schönbein, (h) Andrews.
3. What is the significance of each of the following terms: (a) *oxygen*, (b) *hydrogen*, (c) *ozone*, (d) *phlogiston*?
4. Why does the carburetor on a motor car have to be adjusted according to the temperature in order to secure the best results?
5. Is the statement that 1 l. of oxygen weighs 1.429 g. an exact statement in itself?
6. Distinguish clearly between a law and a theory.
7. State the laws that have been discussed in the preceding chapters.

8. From your experiences, state whether the compression of gases, as well as their expansion, is attended by any change of temperature. Explain fully.

9. Why does a balloon filled with hydrogen gradually lose its buoyancy?

### PROBLEMS

1. A gas measured 150 cc. when subjected to a pressure of 740 mm. What volume would it occupy if the pressure were increased to 760 mm., the temperature remaining constant?

2. A gas subjected to atmospheric pressure measured 750 cc. when the barometric reading was 740 mm. What volume would this gas occupy if transported to a mountain top where the barometric reading was 650 mm., supposing the temperature to remain constant?

3. (a) A gas measured 150 cc. in a laboratory in which the temperature was  $18^{\circ}$ . What would be the volume of the gas if the temperature were reduced to  $0^{\circ}$ , the pressure remaining constant? (b) Suppose that the temperature were increased from  $0^{\circ}$  to  $273^{\circ}$ , what volume would the gas then occupy?

4. A certain weight of hydrogen, subjected to atmospheric pressure, occupied a volume of 1250 cc. in a laboratory in which the readings of the thermometer and barometer were  $18^{\circ}$  and 746 mm. respectively. What volume would this gas occupy under standard conditions?

5. A gas subjected to atmospheric pressure occupied a volume of 1000 cc. in a laboratory at  $20^{\circ}$  and 740 mm. The next day the temperature of the laboratory fell to  $12^{\circ}$ , while the barometric pressure increased to 752 mm. What volume did the gas occupy under these conditions?

6. A cylinder of oxygen at  $20^{\circ}$  showed a pressure of 100 atmospheres. During a fire it became heated to  $600^{\circ}$ . What was the pressure at this temperature?

7. (a) Calculate the weight of 50 l. of oxygen measured at  $25^{\circ}$  and 740 mm. (b) What weight of potassium chlorate would be required for the preparation of this weight of oxygen?

8. A certain volume of gas is measured when the temperature is  $20^{\circ}$ . If the pressure is kept constant, at what temperature will the volume be doubled?

9. Calculate the *relative rate* at which *hydrogen* and *chlorine* will diffuse (see weights of 1 l. of each of these gases in Appendix B).

## CHAPTER V

### WATER; HYDROGEN PEROXIDE

**Historical.** Following the discovery of hydrogen, Cavendish made a careful study of the properties of the gas. In the course of his experiments he exploded a mixture of hydrogen and air and observed that a small amount of a dewlike substance was formed. He repeated the experiment a number of times, on some occasions substituting pure oxygen for air, and thus was able to obtain a sufficient amount of the liquid to make a study of its properties. This liquid proved to be pure water. Cavendish did not perceive the full meaning of his discovery, however, and it remained for Lavoisier, a few years later, to repeat and properly interpret the experiments of Cavendish. He proved beyond doubt that the water which Cavendish had obtained resulted from the union of the hydrogen and oxygen, and pointed out that *water must therefore be regarded as a compound of these two elements.*

**Occurrence.** The great abundance and wide distribution of water are facts familiar to all. Vast areas of the colder regions of the globe are covered with it in the form of ice, while in the liquid state it covers about five sevenths of the earth's surface, reaching in some places a depth of nearly six miles. Large quantities occur in the soil, and as a vapor it is an essential constituent of the atmosphere. It likewise constitutes more than half the weight of living organisms. For example, nearly 70 per cent of the human body is water. The water content of some of the more common foods is given in the table on page 457.

**The composition of natural waters.** All natural waters contain more or less foreign matter, either in solution or held in suspension. Even the water which falls to the earth in the form of rain contains particles of dust, as well as small quantities of gases

absorbed from the atmosphere. Upon reaching the earth's surface it dissolves mineral matter present in the rocks and soil, such as common salt and compounds of calcium, magnesium, and iron. Waters containing such substances in solution are commonly spoken of as *hard waters* or, if large amounts of mineral matter are present, as *mineral waters*. The quantity and nature of the substances present vary with the nature of the rocks and soil with which the water comes in contact. The weight of such matter present in 1 l. of average well water varies from 0.1 to 0.5 g. Much larger quantities are present in the waters from some springs and very deep wells. The waters of the ocean contain over 8.5 per cent of mineral matter, more than three fourths of which is common salt. In addition to mineral substances natural waters contain more or less organic matter. This consists not only of inanimate matter, derived from the decay of organic bodies on the earth's surface or present in sewage, but also of certain forms of living microorganisms which usually accompany such products. Waters taken from shallow wells or streams in thickly populated districts are likely to contain a considerable quantity of such matter.

**Effect upon health of the foreign matter in water.** Since natural waters constitute the ordinary supply for drinking and household purposes, it becomes of importance to inquire into the effect of the foreign matter in such waters when taken into the system. Experience has shown that the mineral matter commonly found in water is not, as a rule, injurious to health. In fact, the presence of a certain amount of such matter is advantageous, supplying a portion of the mineral constituents necessary for the formation of the solid tissues of the body.

As previously stated, the organic matter present in water consists of inanimate products as well as of living microorganisms. The amount of the former commonly present in a water used for drinking purposes is so small that it is practically without effect upon the system. Of course, if present in large amounts, or if poisonous, as in the case of sewage, sickness would result from

its consumption. On the other hand, *the presence, in water, of any considerable number of microorganisms renders it dangerous as a drinking water.* It is true that many of these organisms are without injurious effect upon the system, but it is likewise true that others are the direct cause of disease. Thus it is known that a transmissible disease such as typhoid fever is due to certain microorganisms which find entrance into the body. It is easily possible for these organisms to find their way, through sewage, from a person afflicted with the disease into a poorly protected water supply, and so contaminate the water. It is largely in this way that typhoid fever is spread. The general conclusion may therefore be drawn that, save in exceptional cases, any sickness traceable to the water supply is due to the presence in the water not of mineral matter or even of inanimate organic matter but of certain living microorganisms.

**The detection of impurities in water.** The total amount of solid matter present in any given water is easily determined by evaporating a definite volume of the water to dryness and weighing the residue. This residue may then be subjected to further investigation and the nature of the mineral matter determined. A statement of the mineral matter present in a water, including the percentages of each kind, is commonly termed a *mineral analysis*. Such an analysis is of importance in determining whether or not a water is adapted for manufacturing purposes, such as for use in a steam boiler. On the other hand, if one wishes to determine whether a water is wholesome for drinking, a so-called *sanitary analysis* is required. Such an analysis includes primarily not only the determination of the organic matter present in the water but also of the decomposition products formed by the decay of such matter (such as ammonia, nitrites, and nitrates).

From what has been said it might be inferred that a bacteriological examination alone would decide the question. While it is true that such an examination is of the greatest importance, yet it is equally true that the determination of the inanimate organic matter present, together with the products of its decomposition,

is of equal value and supplements the knowledge gained from a bacteriological examination; for the disease-producing organisms find their way into a water supply through the sewage or drains, and are therefore accompanied by other organic matter, the presence of which in a water supply at once indicates pollution. Such a water should therefore not be used, for, although it may be temporarily free from disease-producing organisms, the conditions are such that their introduction may take place at any time.

It may be added that the physical properties of a drinking water rarely give any conclusive evidence as to its purity. A water may be unfit for drinking and yet be perfectly clear and odorless. Neither can any reliance be placed on the simple methods sometimes given for testing the purity of water. Only the trained chemist and bacteriologist can carry out such methods of analysis as are trustworthy.

**The removal of foreign matter from natural waters; distilled water.** Inasmuch as all natural waters contain foreign matter, it becomes of interest to inquire into the methods used for removing such matter and so for obtaining chemically pure water. The process employed for this purpose is known as *distillation*, and consists in boiling the water and condensing the resulting steam.

**Laboratory distillation.** As commonly carried out on a small scale in the laboratory the process is as follows: The sample of water is poured into the flask *A* (Fig. 27) and boiled. The resulting steam is conducted through the condenser *B*, which usually consists of a narrow glass tube sealed within a larger one. A current of cold water which is admitted at *C* and escapes at *D* is continuously passed through the space between the two tubes. The inner tube is thus kept cool, and the steam, in passing through it, is condensed and collects in *E*.

The water formed by the condensation of steam is known as *distilled water*. The mineral matter present in the original water, being nonvolatile, remains in the container in which the water is being boiled. The organic matter is also largely left in the container. A small amount of it, however, may be decomposed into volatile products, in which case these pass over with the

steam and are present in the distilled water. The percentage of such matter present in distilled water is so small, however, that it is practically without effect in the chemical processes in which pure water is employed, except in a very few cases where extreme purity is required. If it is desired to remove such traces of foreign matter, the distilled water is treated with certain reagents which combine with the impurities to form nonvolatile compounds, and the process of distillation is

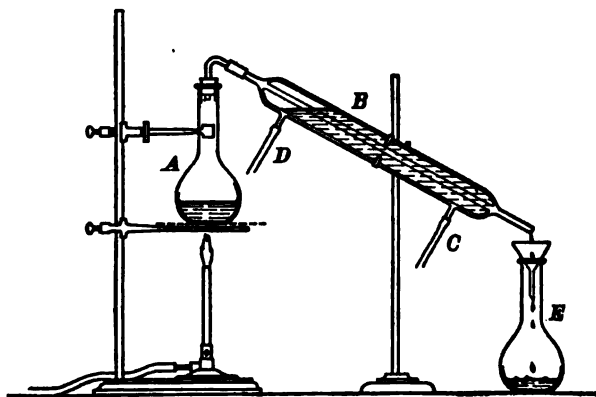


FIG. 27

repeated. In such cases the steam is condensed in a tube made of tin rather than of glass, since this metal is more resistant than glass to the action of steam. For the distillation of water on a large scale the water is heated in a boiler made of copper or iron, and the steam is condensed in a tube made of tin wound into the form of a spiral and surrounded by cold water. Distilled water is used by the chemist and pharmacist for various purposes, especially in the preparation of solutions. It is also used in the manufacture of artificial ice and to a limited extent for drinking.

**The purification of water for sanitary purposes.** By the term *pure water* as commonly used we do not necessarily mean water from which all foreign matter has been removed, but rather

that in which any such matter present is not injurious to health. All foreign matter may be removed by distillation, but this method is often impracticable and there are always cheaper methods that may be employed. The methods actually used depend upon the volume to be purified.

1. *Purification of water on a small scale.* Water used in our homes for drinking and culinary purposes is most readily and effectively purified by boiling it for a few minutes. The high temperature destroys any microorganisms present and so renders the water safe for drinking. Formerly filters were used in which the water was passed over charcoal or through porous cylinders, but these methods have been found to be unreliable and are no longer used to any extent.

2. *Purification of water on a large scale.* Many cities find it necessary to take their water supply from rivers and reservoirs in which the water is more or less contaminated with organic matter. Such a water supply is a source of constant menace to the health of the city. It becomes necessary, therefore, to find some way of effectively purifying the water on a large scale. Two general methods are used for this purpose, namely, (1) treatment with some germicide, usually chlorine gas which destroys the microorganisms present, and (2) filtration. As a rule the two methods are combined. The water is filtered on a large scale by allowing it to drain through large filtration beds prepared from sand and gravel. Some of the impurities are strained out by the filter, while others are decomposed by the action of certain kinds of microorganisms which collect in a gelatinous layer on the surface of the filter. Such filters are known as *slow sand filters*.

Fig. 28 shows a cross section of such a filter bed. The water filters through the sand and gravel and passes into the porous pipe *A*, from which it is pumped into the city mains. The filters are usually covered, to prevent the water from freezing in cold weather.

In some cases the water before filtration is pumped into large tanks and treated with certain compounds, such as alum,

which form in the water a small amount of gelatinous solid. This slowly settles to the bottom of the tank, carrying with it much of the organic matter present. The resulting water is then filtered through a so-called *mechanical filter* composed of sand and gravel. The mechanical filter has largely replaced the slow sand filter, since the process is more rapid and just as effective.

The effect of the filtration of the water supply upon the health of a city is shown by the fact that typhoid fever is

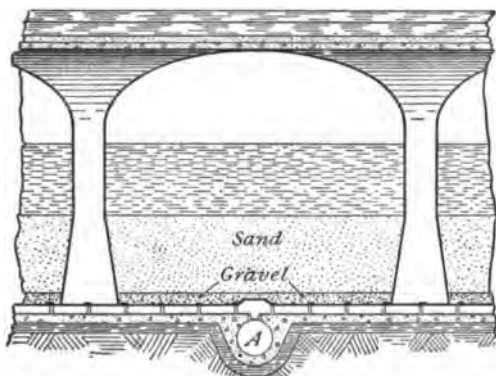


FIG. 28

practically unknown in a city having an effective water purification plant which is the sole supply of water. Water taken from a well in a city is always a source of danger.

**Self-purification of water.** It has long been known that water contaminated with organic matter tends to

purify itself when exposed to the air. For example, the water in a river, made very foul by the introduction of sewage at some point, gradually becomes purer as it flows down the bed of the river. While purification may be influenced by several causes, it is primarily due to the oxidation of the organic matter by oxygen absorbed from the air. Streams of purer water flowing in greatly assist not only by dilution but also by bringing in additional oxygen. As the inanimate organic matter is thus gradually removed, many of the microorganisms die from lack of nutriment or from change in conditions, while others gradually settle to the bottom of the river, especially if the current is slow. This method of purification, however, cannot be relied upon, especially in thickly populated districts, to purify contaminated water so as to render it safe for drinking purposes.

While all microorganisms are destroyed by heat, low temperature has but little effect upon many of them. It follows that ice frozen from impure water may be contaminated and should not be used for household purposes.

**Properties.** At ordinary temperatures pure water is a clear, transparent liquid. It has a slightly bluish color, but this is only noticeable in water of considerable depth, especially in lakes in which the water is fairly pure and deep. It solidifies at  $0^{\circ}$  and boils at  $100^{\circ}$  under the normal pressure. The density of water varies with its temperature, reaching its maximum at  $4^{\circ}$ , as shown in the following table:

TEMPERATURE	DENSITY	TEMPERATURE	DENSITY
$0^{\circ}$	0.9998	$40^{\circ}$	0.9923
$4^{\circ}$	1.0000	$60^{\circ}$	0.9833
$10^{\circ}$	0.9997	$80^{\circ}$	0.9719
$20^{\circ}$	0.9982	$100^{\circ}$	0.9586

Water possesses to a remarkable extent the property of dissolving other substances; indeed, a greater variety of matter is dissolved by water than by any other known solvent. Many substances, such as glass and various kinds of rock, which are ordinarily considered insoluble in water, do, however, dissolve to a very limited extent.

The properties of water, as well as the ease with which the pure liquid can be obtained, render it well adapted for use in the choice of certain units. Thus, its boiling and freezing temperatures are the fixed points used in the graduation of the thermometric scales. Its connection with the unit of mass, as well as of heat, has been referred to in Chapter I. The change of water from any one of the three states, solid, liquid, and gaseous, into any other of these states is always attended by an absorption or liberation of energy in the form of heat. Such energy transformations always accompany changes in state, not only of water but of matter in general. They will therefore be discussed under a single head in the following chapter.

**Chemical conduct.** A knowledge of the chemical conduct of water is of fundamental importance for an understanding of many chemical processes. The main topics to be considered under this head are the effect of heat upon water, the reaction

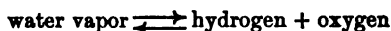
between water and certain elements and compounds, and the part that water plays in promoting chemical changes.

1. *The effect of heat upon water.* We have already seen that it is possible to decompose water either by the action of the electric current or by passing its vapor over some highly heated metal such as iron. It is also of interest to inquire whether the decomposition of water into hydrogen and oxygen can be brought about by heat alone. Experiments have shown that such a decomposition does occur, but only to a slight extent, even at very high temperatures. The following table by Langmuir gives the percentages of the total quantity of water decomposed when heated to the temperature indicated. The results must be considered as only approximate ones, since the experiments are very difficult to carry out:

TEMPERATURE	PERCENTAGE OF WATER DECOMPOSED	TEMPERATURE	PERCENTAGE OF WATER DECOMPOSED
1327°	0.0446	1727°	0.504
1427°	0.0920	1927°	1.21
1527°	0.17	2227°	3.38
1627°	0.302	2728°	11.10

Compounds, like water, which are not readily decomposed by heat are called *stable compounds*.

When water vapor is heated in a closed vessel to a temperature above the point at which decomposition begins, the percentage of the total vapor which is decomposed gradually increases with the rise in temperature. If, however, the temperature is maintained constant at any point, the decomposition *apparently* ceases. In reality, however, it is known that the decomposition continues, but that the oxygen and hydrogen so formed gradually combine again and at such a rate that the quantity of vapor decomposed is exactly equal to that formed by the union of the oxygen and hydrogen. In other words, the water vapor is in equilibrium with its decomposition products, namely, oxygen and hydrogen. The change, therefore, like the change of oxygen into ozone and the reaction between iron and steam, is a reversible one and may be expressed as follows:



2. *The action of certain elements upon water.* Reference has been made to the fact that some of the elements, such as iron, react with water under proper conditions, combining with the oxygen and thus liberating the hydrogen. On the other hand, a few of the elements, such as fluorine and chlorine, have just the opposite action, combining with the hydrogen and liberating the oxygen.

3. *The action of water upon oxides.* Water combines with many of the oxides to form important compounds. It is convenient to divide these oxides into two general classes, according to the nature of the compounds resulting from their union with water: (1) The members of the one class combine with water to form *acids*. This class is represented by such oxides as sulfur dioxide and phosphorus pentoxide, compounds formed by the combustion of sulfur and phosphorus respectively. (2) The members of the second class of oxides, on the other hand, combine with water to form *bases*, to which reference has already been made (p. 47). To this class belong, for example, the oxide of calcium (ordinary lime) which combines with water to form the base known as calcium hydroxide, or slaked lime.

4. *The action of water in the formation of hydrates.* When crystals of ordinary alum are heated, water is evolved, while the crystals crumble to a fine powder commonly known as burnt alum. When this burnt alum is dissolved in water and the resulting solution is allowed to evaporate, there is deposited a crystalline compound, formed by the union of the burnt alum with water, which is identical in composition with the original crystals. Similarly, when the blue crystalline compound known as copper sulfate or blue vitriol is heated, water is evolved, the blue color fading at the same time until there remains a white, powdery residue. As in the case of alum, the blue crystals may again be formed from this residue by dissolving it in water and evaporating the solution. Many other compounds, especially those belonging to the class known as salts, act like alum and copper sulfate, evolving water when heated, but again

combining with it in solution to form the original compound. The compounds which combine with the water are commonly spoken of as *anhydrous* substances, while the compounds formed by their union with water are termed *hydrates*. Thus the blue crystalline compound referred to above is a hydrate of copper sulfate, while the white residue formed on heating this hydrate is the anhydrous copper sulfate. These hydrates are true chemical compounds, any given hydrate being formed by the union of definite weights of the anhydrous substance and water. Thus any given weight of anhydrous copper sulfate always combines with 56.43 per cent of its weight of water to form the ordinary hydrate. Many anhydrous substances, however, combine with different percentages of water to form different hydrates.

The water which combines with compounds to form hydrates is sometimes termed *water of crystallization*, for the reason that many hydrates are crystalline in character and, when heated, lose water, with an accompanying loss of crystalline structure.

It must not be supposed that all crystalline substances contain water of crystallization. The majority of minerals, such as quartz and the diamond, are crystalline without having water of crystallization. Likewise some salts, such as sodium chloride, crystallize from water in the anhydrous form.

The term *water of crystallization* seems to imply the presence of water as such in the crystals. There is no evidence, however, that this is so. That a compound evolves water on being heated is not a proof that the water as such is present in it, since the compound may contain hydrogen and oxygen which unite to form water in the process of decomposition.

**5. The action of water in promoting chemical changes.** Many substances which have no action upon each other in the absence of water readily enter into combination in its presence. The reason for this is not always clear. In some cases the increased activity seems to be due entirely to the fact that when in solution the substances are brought into more intimate contact. On the other hand, all acids, bases, and salts when dissolved in water undergo at least a partial decomposition, and the greater activity of these compounds when in aqueous solution is connected with this fact.

Attention has already been called to the marked catalytic effect of moisture. Even a trace of it often has a marked influence in increasing the speed of certain chemical changes.

**The determination of the exact composition of water.** Many very careful experiments have been made for the purpose of determining, with as great accuracy as possible, the ratio in which hydrogen and oxygen are present in water, and it is worth our while to study somewhat in detail the methods which have been employed, since they serve to illustrate in a general way the methods used in determining the composition of other compounds.

Two general methods of procedure are available for determining the composition of a compound: first, *the method of analysis*, in which a given weight of the compound is separated either directly or indirectly into its constituent elements and the identity and weight of each determined; second, *the method of synthesis*, which consists in determining the proportion in which the constituent elements unite to form the compound, and which is therefore just the opposite of analysis.

**1. Methods based on analysis.** It will be recalled that water may be easily decomposed into its constituents by the electric current. It would naturally seem that the exact composition of water could easily be determined in this way, since the volumes of the gases liberated can readily be measured with accuracy, and, if we know their densities, the weights of the gases so liberated can be calculated. When the experiment is carried out, however, the results obtained are not concordant, although in general the volume of the hydrogen liberated is slightly more than double the volume of the oxygen. Experiments prove that the method is subject to several sources of error. For example, a portion of the oxygen liberated is converted into ozone. Moreover, the water through which the liberated gases bubble (see Fig. 5) dissolves more of the oxygen than of the hydrogen. The ratio between the weights of hydrogen and oxygen obtained in this process, therefore, does not represent with great accuracy the ratio in which they are combined in water. More

accurate results are obtained by a number of synthetic methods such as the ones described in the succeeding pages.

2. *Methods based on synthesis.* In the synthetic methods we determine the quantities of oxygen and hydrogen which combine directly to form water; or we may determine the quantity of either of the elements which enter into the combination, and then determine the weight of the resulting water, the difference

between these two weights being equal to the weight of the other element entering into combination. Three modifications of the method will be described:

(a) *Method used in lecture room.* A description of the method as ordinarily carried out for purposes of illustration in the lecture room will serve to show the general principle involved.

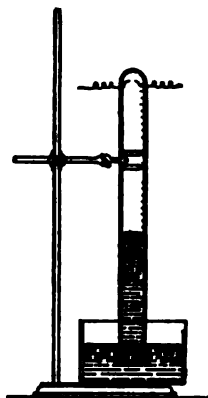


FIG. 29

**The eudiometer method.** In this method the volumes of hydrogen and oxygen combining to form water are directly determined. The combination of the two gases is brought about in a tube called a *eudiometer*. This is a graduated tube about

60 cm. long and 2 cm. wide, closed at one end (Fig. 29). Near the closed end two platinum wires are fused through the glass, the ends of the wires within the tube being separated by a space of 2 or 3 mm. The tube is entirely filled with mercury and inverted in a vessel of the same liquid. Pure hydrogen is passed into the tube until it is about one fourth filled. The volume of the gas is then read off on the scale and reduced to standard conditions. An approximately equal volume of pure oxygen is then introduced and the volume again read off and reduced to standard conditions. This gives the total volume of the two gases. From this the volume of the oxygen introduced may be determined by subtracting from it the volume of the hydrogen. The combination of the two gases is now brought about by connecting the two platinum wires with an induction coil and passing a spark from one wire to the other. Immediately a slight explosion occurs. The mercury in the tube is at first depressed because of the expansion of the gases due to the heat generated in the reaction, but it at once rebounds, taking the place of the gases which have combined to form water. The volume of the water in the liquid state is so small that it may be disregarded in the calculations. In order that the temperature of the residual

gas and the mercury may become uniform, the apparatus is allowed to stand for a few minutes. The volume of the gas is then read off and reduced to standard conditions, so that it may be compared with the volumes of the hydrogen and oxygen originally taken. The residual gas is then tested in order to ascertain whether it is hydrogen or oxygen, experiments having proved that it is never a mixture of the two. From the information thus obtained the composition of water may be calculated. Thus, suppose the readings were as follows:

Volume of hydrogen taken . . . . .	20.3 cc.
Volume of hydrogen and oxygen . . . . .	38.7 cc.
Volume of oxygen . . . . .	18.4 cc.
Volume of gas left after combination has taken place (oxygen) . . . . .	8.3 cc.

The 20.3 cc. of hydrogen have combined with 18.4 cc. minus 8.3 cc. (or 10.1 cc.) of oxygen, or approximately 2 volumes of hydrogen have combined with 1 of oxygen. Since oxygen is 15.88 times as heavy as hydrogen, the proportion by weight in which the two gases combined is 1 part of hydrogen to 7.94 of oxygen.

**Precaution.** If the two gases are introduced into the eudiometer in the exact proportions in which they combine, after the combination has taken place the mercury will rise and completely fill the tube. Under these conditions, however, the tube will be broken by the sudden upward rush of the mercury. Hence, in performing the experiment care is taken to introduce an excess of one of the gases to serve as a cushion.

**A more convenient form of eudiometer.** A form of eudiometer (Fig. 30) different from that shown in Fig. 29 is sometimes used to avoid the calculations necessary in reducing the volumes of the gases to the same conditions of temperature and pressure in order to make comparisons. With this apparatus it is possible to take the readings of the volumes under the same conditions of temperature and pressure and thus

compare them directly. The apparatus is filled with mercury, and the gases are introduced into the tube A. The experiment is carried out as in the preceding one, except that, before taking the reading of the gas volumes, mercury is either added to the tube B or withdrawn from it by means of the stopcock C, until it stands at exactly the same height in both tubes. The gas inclosed in tube A is then under atmospheric pressure. The

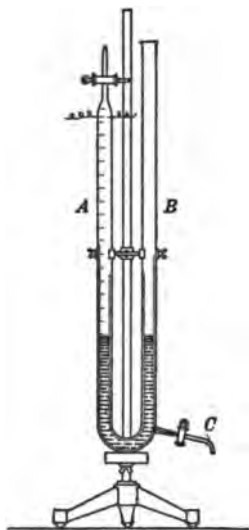


FIG. 30

temperature of the gas, as well as the pressure to which it is subjected, being the same at the conclusion of the experiment as at the beginning, the volumes of the hydrogen and oxygen and of the residual gas may be directly compared as read off from the tube.

(b) *Method used by Berzelius and Dumas.* The work of these investigators is of interest from a historical standpoint, since they were the first to determine the composition of water with any great accuracy. The method used is a very ingenious one, the weights of the hydrogen and oxygen being determined by indirect methods and not by direct weighing of the gases, which is not easily done. The method was first used by Berzelius in 1820 and later in 1848, with greater refinement, by Dumas.

**Experimental details.** Fig. 81 will serve to illustrate the method used by Dumas. Hydrogen is generated in *A* by the action of dilute sulfuric acid on zinc. It is conducted from the generator through the tubes *B* and *C*,

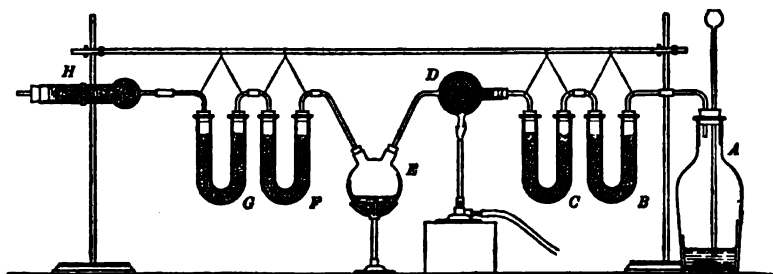


FIG. 81

which are filled with different substances designed to remove all possible impurities from the gas. The pure gas is then conducted into the bulb *D*, which is partly filled with pure copper oxide and kept at a high temperature. A portion of the hydrogen combines with oxygen taken from the copper oxide to form water, most of which is condensed in *E*. The remainder is absorbed by the substance contained in the tubes *F* and *G*. *H* represents a tube filled with some substance which prevents any moisture entering the tube *G* from the air. The weight of the water formed is determined by noting the increase in weight of the bulb *E*, as well as of the tubes *F* and *G*. The weight of the oxygen entering into combination is determined by noting the loss in weight of the bulb *D*, since this loss is due solely to the oxygen taken up from the copper oxide by the

hydrogen to form water. The difference between the weight of the water formed and that of the oxygen in the water represents the weight of the hydrogen. Dumas carried out this experiment nineteen times. He found that the total weight of water formed in his experiments, together with the weights of oxygen and hydrogen present in the water, was as follows:

Total water formed . . . . .	945.439 g.
Total oxygen . . . . .	840.161 g.
Total hydrogen . . . . .	105.278 g.

The relative weights of hydrogen and oxygen in water, as determined by Dumas, are therefore 105.278 : 840.161, or 1 part by weight of hydrogen to 7.98 of oxygen.

(c) *Method used by Morley.* The method used by Morley consists in preparing pure hydrogen and oxygen, and determining not only the weights of the two gases which combine to form water but also the weight of the resulting water.

As the average of twelve experiments, Morley found that the *proportion in which hydrogen and oxygen unite to form water is as follows: by weight, 1 part of hydrogen to 7.94 parts of oxygen; by volume, 2.0024 parts of hydrogen to 1 part of oxygen.*

**Experimental details.** Fig. 32 represents the form of apparatus used by Morley for effecting the combination of hydrogen and oxygen and for weighing the resulting water. Extraordinary precautions were taken to insure pure materials and to eliminate all known sources of error. The air was first removed from the apparatus, which was then sealed and weighed. A tube containing hydrogen absorbed in palladium was weighed and joined to the apparatus at *A*, while a large globe filled with oxygen was weighed and connected at *B*. The two gases were then admitted to the apparatus through the tubes *C, C*, and their union effected as they entered by electric sparks passed between the points at *D*. In order that the resulting steam might be condensed as fast as formed, the apparatus was immersed in cold water during the experiment. After

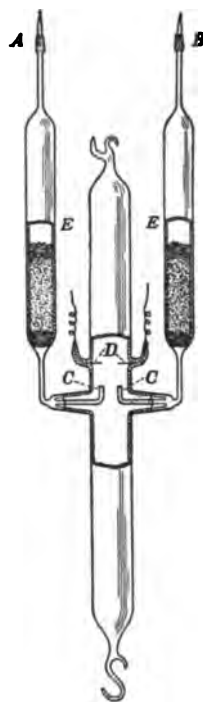


FIG. 32

from 30 to 35 g. of water had thus been formed, the vessels from which the hydrogen and oxygen were supplied were disconnected and again weighed to determine the exact weights of hydrogen and oxygen admitted to the apparatus. There still remained in the apparatus, however, a certain amount of uncombined hydrogen and oxygen which had to be determined. To do this the entire apparatus was immersed in a freezing mixture until the water which had been formed by the union of the hydrogen and oxygen was frozen. The mixture of the uncombined gases was then withdrawn through *A* and *B*. Any moisture present in the mixture was removed as the gas passed through the tubes *E, E*, which were filled with phosphorus pentoxide, a substance which has a strong affinity for water. The weights of hydrogen and oxygen present in the mixture were then determined by analysis. Finally the apparatus itself was weighed, the increase in weight representing the water formed in the experiment.

**Comparison of results obtained.** From the above discussion it is easy to see that it is only by experiment that the composition of a compound can be determined. Different methods may lead to slightly different results. The more accurate the method chosen, and the greater the skill with which the experiment is carried out, the more accurate will be the results. It is universally conceded that Morley's results are the most trustworthy yet obtained.

**Relation between any given volume of aqueous vapor and the volumes of the hydrogen and oxygen which combine to form it.** When the quantitative synthesis of water is carried out at ordinary temperatures, the water vapor formed by the union of the hydrogen and oxygen at once condenses. The volume of the resulting liquid is so small that it may be disregarded in making the calculations. If, however, the experiment is carried out at a temperature of  $100^{\circ}$  or above, the water vapor formed is not condensed, and it thus becomes possible to compare the volume of the vapor with the volumes of hydrogen and oxygen which combined to form it. In this way it has been proved that *2 volumes of hydrogen and 1 volume of oxygen combine to form exactly 2 volumes of water vapor*, the volumes all being measured under the same conditions of temperature and pressure. It will be noted that the relation between these three volumes may be expressed

by whole numbers. The significance of this very important fact will be discussed in a subsequent chapter.

**Apparatus.** The form of apparatus used in determining the relation between the volumes of hydrogen and oxygen uniting and that of the aqueous vapor formed is illustrated in Fig. 33. The arm *A* of the eudiometer in which the combination of the gases is effected is surrounded by a tube through which is passed steam or, preferably, the vapor of some liquid boiling above  $100^{\circ}$  (amyl alcohol is often used). A mixture of 2 volumes of hydrogen with 1 of

oxygen is introduced into the eudiometer. A suitable liquid is then boiled in the flask *B*. The resulting vapor is conducted through the space between the tube *A* and the outer tube, and is then condensed as shown in the figure. When the volume of the mixed gases in *A* has become stationary, showing that the temperature of the

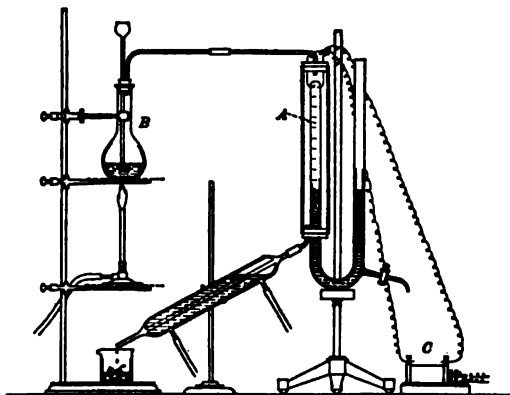


FIG. 33

gases is the same as that of the vapor, and the pressure has been adjusted as in the former experiment (see Fig. 30 and description), the reading on the eudiometer tube is noted. The union of the two gases is then effected by an electric spark from an induction coil *C*, the pressure is adjusted, and the reading again noted after the volume of the vapor has become constant. The volume of the vapor thus obtained can be compared directly with the volumes of the hydrogen and oxygen which united to form it.

## HYDROGEN PEROXIDE

**Composition.** In 1818, while studying the action of acids upon certain oxides, the French chemist Thénard discovered the compound which we now call *hydrogen peroxide*, or sometimes *hydrogen dioxide*. The pure compound is a liquid and, like water, is composed of hydrogen and oxygen. The proportions in which the hydrogen and oxygen are present in these

two compounds, however, are widely different, as is shown in the following statement:

Water . . . . . 1 part of hydrogen to 7.94 parts of oxygen by weight  
 Hydrogen peroxide . 1 part of hydrogen to 15.88 parts of oxygen by weight

In other words, the weight of oxygen combined with a fixed weight of hydrogen is just twice as great in hydrogen peroxide as in water. This larger percentage of oxygen is indicated by

the name *peroxide*, the prefix *per* meaning "more" or "excess."

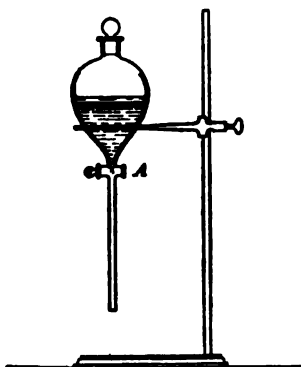


FIG. 34

**Preparation.** While a dilute solution of hydrogen peroxide may be obtained easily, the pure compound cannot be prepared without great difficulty, since it decomposes readily into water and oxygen. Dilute solutions of the compound are prepared by the action of acids upon certain oxides in the presence of water. The oxide commonly used is barium peroxide.

For the acids one may conveniently use either sulfuric or phosphoric acid, properly diluted with water. With sulfuric acid the reaction may be represented as follows:

sulfuric acid + barium peroxide  $\longrightarrow$  barium sulfate + hydrogen peroxide

hydrogen
sulfur
oxygen

barium
oxygen

barium
sulfur
oxygen

hydrogen
oxygen

**Details.** It will be noted that in this reaction the barium of the barium peroxide exchanges place with the hydrogen of the acid. The barium sulfate formed is insoluble, while the hydrogen peroxide dissolves in the water present. The barium sulfate may therefore be removed from the solution by filtration. Phosphoric acid acts in a similar way. In this way one can readily prepare a dilute solution of the peroxide in water. To concentrate this, the solution is transferred to a separatory funnel (Fig. 34), ether is added, and the contents thoroughly shaken. The hydrogen peroxide, being more soluble in ether than in water, is largely dissolved by the ether. On standing, the ether rises to the surface of the

water, carrying with it the dissolved hydrogen peroxide. This solution is then separated from the water by allowing the latter to run out through the stopcock *A*, and the ether is evaporated. Since the boiling point of ether is 34.6°, it is possible to remove it at a comparatively low temperature, and thus to prevent any marked decomposition of the hydrogen peroxide. By distilling off the ether under diminished pressure the separation may be effected at a still lower temperature. In this way, with proper precaution, one can obtain a solution containing nearly 90 per cent of the peroxide. On cooling this solution with a freezing mixture, clear crystals of the pure hydrogen peroxide (melting at  $-2^{\circ}$ ) separate. The pure substance is seldom prepared, because of its highly explosive character.

**Properties.** Hydrogen peroxide is a clear, sirupy liquid having a density of 1.458. It cannot be distilled under ordinary atmospheric pressure, since it decomposes into water and oxygen with explosive violence before the boiling point is reached. Under greatly diminished pressure, however, it may be distilled with little decomposition; thus at a pressure of 29 mm. it boils at 69°. The decomposition of the peroxide is attended by the evolution of heat amounting to 676 cal. for each gram decomposed. It mixes with water, ether, and alcohol in all proportions.

Since hydrogen peroxide so readily decomposes, with evolution of oxygen, it acts as a strong oxidizing agent, even in very dilute solutions. An easily oxidizable substance, like wool, is ignited by the addition of a few drops of the pure compound. The speed of decomposition of hydrogen peroxide is affected by many conditions. In dilute solutions and at a low temperature the speed is very slow, while at higher temperatures and in more concentrated solutions it becomes so great as to cause violent explosions. Moreover, the speed of decomposition is greatly affected by the presence of certain catalytic agents. Thus a little finely divided platinum or manganese dioxide, added to a concentrated solution of the peroxide, produces such rapid decomposition as to cause an explosion. Certain organic substances have a similar action. Just as some substances increase the rapidity of decomposition, so others retard it. Thus the ordinary solution of hydrogen peroxide sold for medicinal

purposes contains a small amount of some such substance, generally a trace of acid, which is added to preserve the strength of the solution by retarding decomposition.

**Illustrative.** The strong oxidizing properties of hydrogen peroxide may be shown by its action upon lead sulfide. This is a black compound of lead and sulfur. When treated with hydrogen peroxide it is oxidized to a compound of lead, sulfur, and oxygen known as lead sulfate, which is white. Through the action of the hydrogen peroxide, therefore, the black color of the lead sulfide gradually gives way to the white color of the lead sulfate.

**Uses.** Hydrogen peroxide has many commercial uses, all based on its strong oxidizing properties. The common medicinal peroxide of the druggist is an aqueous solution containing 3 per cent, by weight, of the compound. This solution has been largely used as a germicide, but recent experiments indicate that it has little, if any, value for this purpose. Like ozone, it acts upon certain dyes and natural colors, such as that of the hair, oxidizing them into colorless compounds; hence it is sometimes used as a bleaching agent. The chemist finds it especially useful as an oxidizing agent in many analytical operations. For this purpose it is often convenient to have a rather concentrated solution, so that a 30 per cent solution is now sold as a commercial product.

### QUESTIONS

1. State clearly the definite reasons for regarding water as a compound rather than as an element or a mixture.
2. Distinguish clearly between (a) oxidation and reduction; (b) oxidizing agent and reducing agent; (c) analysis and synthesis.
3. Discuss the relative advantages of the methods used by Berzelius and by Morley for the determination of the composition of water.
4. How could you tell whether a given sample of water was hard water or distilled water?
5. Suppose that water reached its maximum density at 0°. Mention some effects that would be to our advantage and others to our disadvantage.

6. Define the following terms: (a) *anhydrous*, (b) *hydrates*, (c) *distillation*, (d) *water of crystallization*, (e) *catalytic agent*, (f) *electrolysis*.

7. How could you tell whether or not the water evolved on heating some substance was present in the substance in a free or a combined state?

### PROBLEMS

1. Determine the composition of water from the following data, all volumes given being measured under the same conditions of temperature and pressure.

Volume of hydrogen in eudiometer (Fig. 30)	. . .	19.84 cc.
Volume of hydrogen and oxygen in eudiometer	. . .	48.23 cc.
Volume of gas (oxygen) left after explosion	. . .	19.22 cc.

2. Morley found the composition of water by determining the weights of hydrogen and of oxygen that combine with each other to form water. The results of four trials are as follows:

Hydrogen used	Oxygen used	Hydrogen used	Oxygen used
(1) 3.2645 g.	25.9176 g.	(3) 3.8193 g.	30.3210 g.
(2) 3.2559 g.	25.8531 g.	(4) 3.8450 g.	30.5294 g.

In each case calculate the ratio in which the hydrogen and oxygen combined to form water.

3. The results of some of the individual experiments performed by Dumas in the determination of the composition of water are as follows (p. 82):

Oxygen used	Water obtained	Oxygen used	Water obtained
(1) 13.179 g.	14.827 g.	(3) 60.031 g.	67.586 g.
(2) 76.364 g.	85.960 g.	(4) 20.362 g.	22.905 g.

Calculate the composition of water as determined in each of the trials.

4. 1 l. of water measured at 20° will yield how many liters of oxygen measured at 20° and 760 mm.?

5. What quantity of heat measured in calories is set free in the decomposition of 100 g. of hydrogen peroxide?

6. (a) What volume of oxygen measured at 20° and 740 mm. is evolved in the decomposition of 1 kg. of the ordinary hydrogen peroxide of the druggist? (b) What amount of heat is evolved in this decomposition?

## CHAPTER VI

### THE STATES OF MATTER

**The states of matter.** The study of water has brought to our attention a substance existing in three very different states, gaseous, liquid, and solid. In a general way a *gas* or *vapor* may be regarded as matter in such a state that it distributes itself uniformly throughout the space in which it is placed. A *liquid* does not so distribute itself; it has no characteristic shape of its own, however, but takes the form of the vessel in which it is placed. A *solid* retains its own shape irrespective of the size or form of the containing vessel. The occurrence in all of these three states is not peculiar to water but is found to be true of the great majority of substances. It will therefore be of advantage to obtain a more accurate idea as to the difference between these states, and of the conditions under which a substance may pass from one to another.

#### I. THE RELATION BETWEEN LIQUIDS AND GASES

We shall first consider the relation between liquids and gases.

**Evaporation.** When a liquid such as water is placed in an open vessel, it gradually passes into the air in the form of gas, the process being called *evaporation*. If it is in a confined space, which it only partially fills, as, for example, in a closed bottle, evaporation proceeds until the air above the liquid contains a definite percentage of gaseous water, and then apparently ceases, the air being said to be *saturated* with water vapor. It is only *apparently* that the process ceases as we can easily see if we consider the matter from a kinetic point of view. We may imagine the particles of the liquid to be in motion but moving more slowly than in a gas, with very frequent

collisions and subject to very considerable mutual attraction. From the surface of the liquid the more rapidly moving particles will from time to time escape, breaking free from the attraction of the liquid. They will then move about in the space above the liquid as gas particles, and will from time to time return to it. When the rate at which they escape is equal to the rate at which they return, a state of balance or equilibrium will be reached and there will be no further apparent evaporation. The air above the liquid is now said to be *saturated* with the vapor.

**Effect of temperature upon evaporation.** If the liquid is now warmed, the rate of motion of its particles is increased, more of them break free from the surface, and consequently the rate of evaporation is increased. A new equilibrium is reached at the higher temperature, there being a larger percentage of the gaseous substance in the air than before. The quantity of water present in gaseous form over water in a closed space is therefore roughly proportional to the temperature, but experiment shows that it is not accurately so. For exact values we must consult tables based on experiment, or curves plotted from such experiments.

**Vapor pressure.** The quantity of water present in air in gaseous form may be expressed in a number of ways. The Weather Bureau expresses it as *relative humidity*, meaning by this term the quantity present as compared with the quantity which would be present at the same temperature when equilibrium is reached — that is, at saturation. It might be stated simply as the weight in grams in a liter of air.

A more satisfactory way is to express the quantity of water vapor in terms of the pressure which it exerts as a gas. Of the total pressure of the air on the surface of the water a part is due to oxygen, a part to nitrogen, and a part to gaseous water. The quantity of each of these gases is proportional to the pressure which it exerts. We may therefore indicate the fraction of the total pressure due to gaseous water, and so have a convenient method of expressing the quantity of water present in the air, which will be independent of the volume. Owing

to this method of expression the value of the water in the gaseous form at a given temperature is called the *vapor pressure*, or *aqueous tension*, of the water. It would be more accurate to call it the pressure of the vapor that is over the water since the water exerts no pressure. The vapor pressure of a liquid may therefore be defined *as the pressure upon its surface exerted by its own vapor*. A table showing the vapor pressure of water at various temperatures will be found in the Appendix.

**Example.** Air confined over water at 20° will take up water until the water vapor exerts a gas pressure equal to 17.51 mm. If the total pressure of the air is then 760 mm., 17.51 mm. is due to water vapor and 742.49 mm. to other gases. Therefore  $\frac{17.51}{760}$  of the total volume of the air is water vapor. If this volume is 1000 cc.,  $\frac{17.51}{760} \times 1000 = 23$  cc. is the volume the water vapor would itself occupy as a gas at 760 mm. pressure and at 20°.

**Correction for vapor pressure in gas measurements.** If a gas is collected over water, it is evident that the observed volume includes not only that of the gas but also that of the water present as vapor. This latter volume could be calculated in the way just indicated, and deducted from the observed volume of the gas. A more convenient method, especially if the gas volume is to be reduced to standard conditions, is to subtract the value of the vapor pressure at the observed temperature from the pressure under which the gas is measured. This gives the pressure (at the observed volume) that the gas would exert if the water vapor were not there. The formula for reduction to standard conditions (p. 61) will then be

$$V_s = \frac{(P - a) \times V \times 273}{760 \times T},$$

in which  $a$  is the value of the vapor pressure of water at the temperature of observation.

**Determination of vapor pressure.** Experimentally the value of the vapor pressure of a liquid at any temperature may be determined in the following way: Two long barometer tubes are filled with mercury and inverted in

an open vessel of the same liquid (Fig. 35). A few drops of the liquid to be examined are introduced under the open end of one of the tubes, the liquid so introduced immediately rising to the top of the mercury column. Evaporation at once takes place and, because of the pressure of the gas so formed, the mercury column falls to some extent. When equilibrium is reached, the difference in level of the mercury in the two tubes, included between the dotted lines *A* and *B* in the figure, will correspond to the vapor pressure of the liquid expressed in millimeters of mercury. The tubes may be surrounded by jackets through which heated liquids are circulated, so that any desired temperature may be secured.

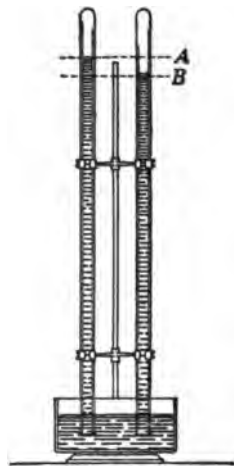


FIG. 35

**Boiling point.** During the heating of a liquid a portion of the energy imparted to it goes to raise its temperature and a portion to change it into a vapor at its surface. When the pressure of the vapor arising from the liquid just exceeds the opposing atmospheric pressure, all the heat energy goes to change the liquid into vapor and into mechanical work in pushing back the atmosphere, and the temperature remains constant. This temperature is called the boiling point under the pressure in question. *The boiling point may be defined as the temperature at which the vapor pressure of the liquid just equals the opposing pressure of the atmosphere.* Since the boiling point depends upon the atmospheric pressure, it is necessary to adopt a standard pressure under which it shall be measured, and this is taken as that exerted by a column of mercury 760 mm. in height, or 1033 g. per square centimeter. Under 760 mm. pressure, water boils at 100°; under a pressure of 525.8 mm., at 90°.

**Formation of bubbles.** We usually think of a liquid as boiling when bubbles form and rise freely through it, and this is really an accurate test, as will be seen by reference to Fig. 36. The figure represents a vessel in which water is being heated under an atmospheric pressure of 760 mm. Suppose a bubble of water vapor is formed at *A*. The pressure upon the bubble will be 760 mm. plus the weight of the water above it. In order that

the bubble may survive, the pressure of the vapor within it upon the inclosing water must exceed the pressure of the water upon the bubble. At  $50^{\circ}$  (the side *B*) a bubble forming at the bottom and moving up through the colder liquid has not enough vapor pressure to balance the opposing pressure, and it gradually collapses. At  $100^{\circ}$  (side *C*) the vapor pressure of the bubble exceeds the external pressure; it is not cooled as it rises, but increases in size as the pressure diminishes, and finally escapes from the surface. The formation and escape of vapor from within the liquid absorbs

all the heat applied, and there can be no further rise of temperature at that pressure.

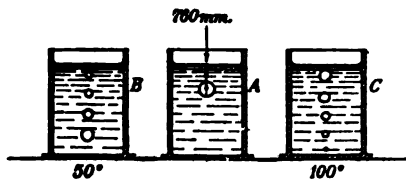


FIG. 36

**Heat of vaporization and condensation.** The quantity of heat absorbed in changing 1 g. of a liquid at its

boiling point into 1 g. of vapor at the same temperature is called the *heat of vaporization*. For water this is unusually large and amounts to 539.1 cal. Conversely, if a gas is maintained at a pressure of 760 mm. and is gradually cooled, condensation to the liquid state begins when the boiling point is reached. During liquefaction the temperature remains constant, and a quantity of heat is given out exactly equal to the heat of vaporization. This is called the *heat of condensation*.

**Critical point.** At high temperatures gases may be subjected to the greatest possible pressure without passing into the liquid state. Thus, if steam is heated above  $360^{\circ}$ , thousands of atmospheres of pressure will not liquefy it. If, while holding the gas under a high pressure, the temperature is slowly lowered, a definite point is reached at which the gas suddenly liquefies. This temperature is called the *critical temperature*, and the pressure required to cause liquefaction at the critical temperature is called the *critical pressure*. The critical pressure is not in general more than about 60 atmospheres. If 100 atmospheres of pressure does not liquefy a gas, it is probably useless to increase the pressure, a lower temperature being the necessary condition. The relations of critical temperature and pressure were discovered by

Andrews in 1869, during his researches on carbon dioxide. Prior to that time thousands of atmospheres of pressure had been applied to oxygen gas in an effort to liquefy it, but to no purpose, since it was much above its critical temperature.

	BOILING POINT	CRITICAL TEMPERATURE	CRITICAL PRESSURE
Hydrogen . . . . .	- 252.7°	- 241°	15 atmospheres
Nitrogen . . . . .	- 195.7°	- 146°	33 atmospheres
Oxygen . . . . .	- 183°	- 118°	50 atmospheres
Sulfur dioxide . . . . .	- 8°	+ 157°	78 atmospheres
Water . . . . .	+ 100.0°	+ 360°	195 atmospheres

**Surface tension of liquids.** We know that heat is absorbed when a liquid evaporates, and that this means the expenditure of energy against some force. So we imagine that the small particles (molecules) of which the liquid is composed have a strong attraction for each other. This force of attraction holds them together in a compact body in opposition to their kinetic motion that otherwise would tend to drive them into the gaseous state.

At the surface of the liquid a peculiar state prevails. The particles on the surface are attracted by those below and on the sides, but there are very few above the surface to pull them forward. They are therefore held in the surface. These attractive forces tend to draw the liquid into a body of the smallest possible volume, namely a sphere, and it requires the expenditure of energy to enlarge the surface against these attractive forces. The force acting parallel with the surface, and tending to diminish its extent, is called *surface tension*.

**Surface tension and the critical point.** As we heat a liquid we stimulate the motion of the particles, but we do not alter their attraction for each other. When their kinetic energy is so great that the force of attraction is completely overcome, there can be no surface tension, and the whole body of the liquid acts as a gas. This is really what takes place at the critical temperature

and is the reason why no amount of pressure will change the gas into a liquid, even though it forces the gas into a space no larger than would be occupied by the same amount of matter in the liquid state.

**Viscosity of liquids.** Some liquids flow very freely and drop from tubes of small bore in very little drops. Others flow slowly and tend to form large drops. This resistance to flow is called *viscosity*, the opposite term being *fluidity*. A slow-flowing liquid is said to have high viscosity, or to be *viscous*.

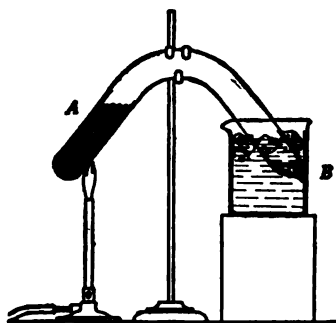


FIG. 37

#### Methods of liquefaction of gases.

The earliest systematic efforts at liquefaction of gases were those of the English scientist Faraday, beginning about 1823. He relied upon the effect of pressure together with moderate cooling, most of his experiments being carried out in the following way: A quantity of solid material which, when heated,

would liberate a considerable quantity of the gas to be liquefied, was placed in one end of a bent tube. The other end was sealed and the tube arranged as shown in Fig. 37, *A* being the solid material and *B* a bath of ice water. Upon heating, the gas is given off in a confined space and, being under great pressure, liquefies in the cold portion of the tube. In this general way Faraday liquefied a number of gases, such as ammonia and carbon dioxide.

Later experimenters made use of much lower temperatures. These low temperatures were secured by taking advantage of the heat of vaporization of low-boiling liquids. When a quantity of any gas, such as sulfur dioxide, is liquefied by pressure, cooled, and then allowed to boil away under the pressure of the atmosphere or in a partial vacuum, the temperature of the liquid falls to its boiling point under that pressure. The very cold, boiling liquid may be used as a bath to cool some other

gas below its critical temperature, when it may in turn be liquefied by pressure. By employing such a process, Cailletet, in 1877, first liquefied oxygen.

Since 1895 purely mechanical methods have been employed in liquefying such gases as air. Machines constructed for this purpose depend for their efficiency upon the cooling effect produced when a highly compressed gas is allowed to expand freely. When a gas is compressed, heat is liberated, and when it is allowed to expand, heat is absorbed. The two quantities of heat are not quite equal, for when the gas is compressed, the attraction of the gas particles for each other *assists* the external pressure, but the same forces in the compressed gas tend to *prevent* expansion. Both these effects are in the same direction, and this causes the heat absorbed in expansion to be slightly more than that given off during compression.

When a gas is alternately compressed and expanded, its temperature steadily falls to the point of liquefaction.

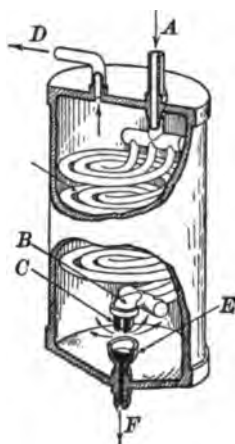


FIG. 38

**The Hampson liquefier.** The essential features of the Hampson type of liquefier are shown in Fig. 38. The air, compressed to about 200 atmospheres by a compressor engine and cooled by running cold water, enters the liquefier at *A*. The tube *A* divides into three or four small copper tubes wound in spirals of many turns so as to fill the cylindrical housing of the liquefier as full as possible with a mesh of tubes having a very large surface. These small tubes reunite into the tube *B*, which is provided with a needle valve at *C* through which the compressed air escapes and expands to atmospheric pressure. In doing so it becomes very cold and is led back over the mesh of spiral tubes, cooling them and their contents of compressed air, and finally leaves the liquefier at *D*. It then goes to the compressor and is once more compressed. During the process the air within the small tubes becomes colder and colder until some of it drops through the needle valve as a liquid and collects in the cup *E*, from which it can be drawn off from time to time through the tube *F*.

**Dewar flasks.** For collecting and temporarily preserving such liquids Dewar employed a special type of vessel which has come to be known by his name. This consists of two concentric vessels of any convenient shape, such as the one shown in Fig. 39. The two flasks are joined together at the upper rim only, and the space between them is exhausted by an air pump. A vacuum serves as the best possible insulator to heat conduction, and the surface of the outer flask may also be silvered, so that external heat may be reflected from it and not absorbed. Liquid air may be preserved in such a vessel for many hours. Thermos bottles of the same plan of construction are now familiar utensils for keeping liquids either hot or cold during long journeys, and are very effective.

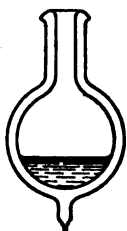


FIG. 39

## II. THE RELATION BETWEEN LIQUIDS AND SOLIDS

Let us now consider the relation between liquids and solids.

**Solid bodies.** When a pure liquid is cooled sufficiently, it usually reaches a temperature at which a sudden change begins, the liquid gradually freezing to a mass of crystals, while the temperature remains constant. With water this takes place at zero. Some liquids, such as waxes, glasses, and glues, simply become less and less fluid and do not have any definite point of solidification. They finally reach a condition in which they are apparently solids. It has been found that those solid substances which have a crystalline structure have a sharp solidifying point, while noncrystalline, or *amorphous*, substances pass gradually from undoubted liquids into what appear to be rigid solids, with no sharp temperature of transition. These are best regarded as still liquids but so viscous as to be quite rigid, the term *solid* being reserved for crystalline bodies having a sharp solidifying point.

**Melting point.** When a crystalline solid is slowly heated, the temperature steadily rises to a certain definite point. Further

application of heat does not raise the temperature, but the solid begins to melt. The temperature remains constant until the melting is complete, and then rises again. The heat energy supplied during the process of melting has no effect on the temperature, but is used up in altering the physical state of the substance. The quantity of heat absorbed in converting 1 g. of a solid at its melting point into 1 g. of liquid at the same temperature is called the *heat of fusion* of the substance. For ice this amounts to 80 cal., which is larger than that for most solids.

**Freezing point.** When a liquid is cooled it does not always begin to solidify when the melting point is reached. It may be cooled considerably below that point, and the liquid is then said to be *undercooled*. This happens to water in a shallow pool on a cold, still night. If now a fragment of the solid is placed in the liquid, or if the liquid is violently shaken, solidification at once begins, the temperature rising to the true freezing point and remaining constant. *The freezing point is therefore most accurately defined as the temperature at which the liquid and the solid will remain unchanged in contact with each other.* The more viscous a liquid is at its freezing point, the more readily undercooling takes place; and with very viscous liquids, as we have seen, true solidification may never occur.

In the process of solidification heat is given out corresponding to the heat of fusion. In both cases it will be noticed that the energy change opposes the physical change taking place. The evolution of heat during solidification retards the freezing, for it is only as this heat is lost by radiation that the solidification can continue. Were it not for this, ponds would freeze very rapidly in winter when the freezing point is reached. Amorphous bodies have no point at which we can detect a corresponding evolution or absorption of heat, which is another reason for regarding them as liquids, even when they are apparently solids.

**Vapor pressure of solids.** Many solids give off vapor at ordinary temperatures, just as do liquids. This is evident from the odor of such solids as camphor and naphthalene (moth balls).

As the solid is heated this vapor pressure increases in value. If it increases to the point where it just exceeds the pressure of the atmosphere, the solid passes directly into a gas without melting or boiling. This is the case with quite a number of solids, such as solid carbon dioxide whose vapor pressure reaches 760 mm. at  $-78.5^{\circ}$ , but which does not melt until  $-56^{\circ}$ . At this point its vapor pressure is more than five atmospheres. When the vapors from such solids are cooled, they pass directly back into the solid form. The process of converting a solid into a vapor and cooling the vapor to a solid again is called *sublimation*, and the solid is said to *sublimate* on heating. It will be remembered that the corresponding process with liquids is called *distillation*. Solids which have a sufficient vapor pressure are often separated from nonvolatile impurities by sublimation, and this has given rise to such names as *corrosive sublimate* (mercuric chloride).

**Equilibrium diagram.** In the preceding pages we have seen that a number of different conditions of equilibrium are capable of existing between the several physical states of a given substance. Thus, with water we have an equilibrium between the vapor and the liquid; between the vapor and the solid; between

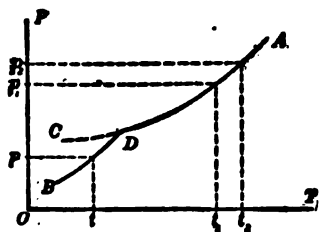


FIG. 40

the liquid and the solid. At every different temperature there is a different pressure exerted by the vapor on the liquid or the solid. We can represent all these relations in a very compact form in a diagram (Fig. 40) in which we represent temperature by distances along the line  $OT$  and pressure by distances

along the line  $OP$ . The curve  $DA$  represents the increase of vapor pressure of the liquid with rise in temperature, the vapor pressures  $p_1$ ,  $p_2$  corresponding to the temperatures  $t_1$ ,  $t_2$ . This curve ends at a point  $A$ , which is the critical temperature at which the distinction between liquid and vapor abruptly ceases.  $DB$  is the vapor-pressure curve of the solid, usually called the sublimation

curve, the pressure  $p$  corresponding to the temperature  $t$ . The point  $D$ , where these two curves intersect, is the freezing point of the liquid, the vapor pressures of solid and liquid being equal. Since the two curves intersect at this point, the solid and liquid can coexist at this temperature and pressure, but they can do so at no other point; this is therefore called a *transition point*. If no solid makes its appearance at the freezing point, the vapor pressure of the liquid will be represented by the extension of the curve  $AD$  toward  $C$ . It will be seen that the vapor pressure of under-cooled liquid is greater than that of the solid at the same temperature, as at  $t$ , indicating a more unstable condition. Very few solids can be heated above the melting point without melting, so the curve  $BD$  can rarely be prolonged beyond the transition point.

**Crystals.** When a liquid freezes it changes into a mass of solid bodies, each of which has a definite geometric form and is known as a crystal. Similar bodies may also be deposited from solutions or be formed by condensing vapors. A crystal is always bounded by plane surfaces, which are arranged in an orderly fashion with reference to imaginary lines drawn through the crystal and called its axes. Every crystal has therefore a definite geometric form. While the variety of form which crystals may assume is almost endless, it has been found that they may all be referred to one of six fundamental arrangements of axes, these constituting what are known as the systems of crystallography. These arrangements, together with two of the simplest crystal forms referred to each, are shown in the accompanying figures (Figs. 41-47).

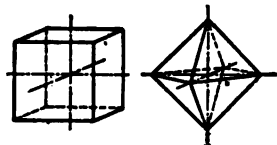


FIG. 41

**The crystal systems.** The relation of the axes in the several systems is as follows:

1. Isometric or regular system (Fig. 41): three equal axes all at right angles to each other.
2. Tetragonal system (Fig. 42): two equal axes and a third of different length, all at right angles.
3. Orthorhombic system (Fig. 43): three unequal axes all at right angles.

4. Monoclinic system (Fig. 44): two axes at right angles and a third at right angles to one of these but inclined toward the other. The axes may be of any relative lengths, and the angle of inclination may vary from  $0^\circ$  to  $90^\circ$ .

5. Triclinic system (Fig. 45): three axes, all inclined toward each other. The axes may be of any relative lengths, and the angles of inclination may also vary.

6. Hexagonal system (Fig. 46): three equal axes in the same plane, intersecting at angles of  $60^\circ$ , and a fourth at right angles to all of these. In

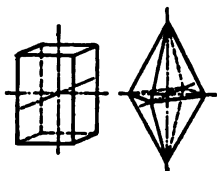


FIG. 42

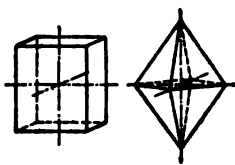


FIG. 43

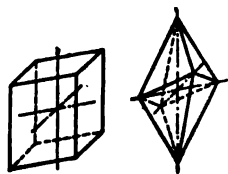


FIG. 44

addition to the two general forms shown in Fig. 46 there are many rhombic forms belonging to this system, such as the one represented in Fig. 47.

**Structure of crystals.** There is little doubt that these plans of formation correspond to orderly arrangements of the particles of solid matter of which the crystals are composed, so that the crystals resemble in structure the piles of cannon balls in a military park. In accordance with this idea it is known that the various properties of the crystal, such as hardness, strength, optical refraction, and conductivity toward heat and electricity, differ in different directions through the crystal. Crystals also split in

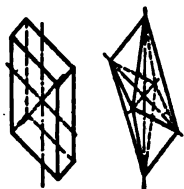


FIG. 45

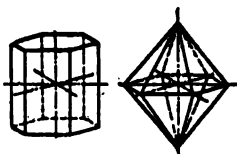


FIG. 46



FIG. 47

definite directions, giving plane surfaces. Some of these groupings represent a more stable arrangement than do others, so that when a given substance crystallizes in two forms, as sometimes happens, the change from the one to the other is in general accompanied by an energy change. It is evident that a body like glass might be cut and polished so as to be an exact copy of a crystal, but would really not be one at all, since it would have none of the structure of a crystal.

**Crystal form a characteristic of a substance.** In general, under the same conditions, a given substance will always crystallize in a form which may be referred to the same system and with the same ratio of axis lengths and degree of inclination. The actual crystal form may be quite different, however. For example, the form may be either a cube or an octahedron, both of which are referred to the same axes. Not infrequently a substance may, under different conditions, assume two forms in entirely different systems, and it is then said to be *dimorphous*. For example, one form may occur when the substance freezes, and another when it is deposited from solution. *Trimorphous* substances are also known. When two substances crystallize in the same form and have the same inclination of axes and the same ratios in their lengths, they are said to be *isomorphous*.

### QUESTIONS

1. Is it correct to say that the boiling point of a liquid is the temperature at which the liquid passes into a vapor?
2. Why does blowing air across the surface of water contained in an open vessel cool the water?
3. In Faraday's method of liquefying gases what produces the pressure?
4. (a) Do the particles of a gas have any attraction for each other? (b) What evidence can you give for this?
5. How do you account for the fact that a thermos bottle will keep a hot liquid hot and a cold liquid cold?
6. Why does ice melt so slowly even when the temperature of the air is considerably above the freezing point?
7. Why do vegetables cook faster in a vessel from which the steam cannot escape than in an open vessel?
8. Why does one seem to perspire more in a moist climate than in a dry one, assuming that the temperature is the same in both cases?
9. Will ice melt faster on a windy day or on a still one, assuming that in each case the temperature is the same degree above freezing?
10. From the energy standpoint, what becomes of the heat absorbed during fusion?

## PROBLEMS

1. Suppose a 10-liter bottle has been standing half full of water at  $30^{\circ}$ , the barometer reading 750 mm. (a) What is the partial pressure of the water vapor in the air above the water? (b) If this water vapor could be obtained as a pure gas at this temperature and pressure, what volume would it have?

2. Suppose 100 g. of steam at  $100^{\circ}$  were to be condensed by passing it into 1000 g. of water at  $20^{\circ}$ . What would be the final temperature?

3. Suppose a fermentation took place in a refrigerator that evolved 100,000 cal. How much ice would this melt?

4. A certain weight of ice at  $0^{\circ}$  was changed into steam at  $100^{\circ}$ . 100,000 cal. of heat were required. What was the weight of the ice?

5. A volume of air standing over water at  $20^{\circ}$  and 750 mm. measured 2000 cc. Calculate its volume when dry at the same pressure (a) by computing the volume of the water vapor and subtracting; (b) by subtracting the aqueous tension from the pressure and calculating the volume under 750 mm. of dry air. (c) How do the two results agree?

6. 1 kg. of water at  $30^{\circ}$  was cooled by the addition of 200 g. of ice at  $0^{\circ}$ . What was the resulting temperature, upon the supposition that no heat was lost by radiation?

## CHAPTER VII

### THE LAWS OF CHEMICAL COMBINATION ; THE ATOMIC THEORY

**I. Fundamental laws of chemical combination.** Having considered two typical elements, and having gained some insight into chemical reactions through a study of the preparation of these elements and the combinations which they form with each other and with other elements, we may now go on one step farther. What generalizations have been reached in regard to the characteristics of chemical action? What theories have been developed to account for the laws that have been found? These are the questions which suggest themselves and which we shall now consider. Aside from the question of energy relations, our knowledge of chemical action may be stated in the form of four general laws.

1. *The law of conservation of mass.* In the earlier stages of the development of chemistry little importance was attached to the relations by weight between reacting substances. In a general way it was assumed that the total weight remained constant, but as heat, light, and phlogiston (the principle of combustion) were all considered to have weight, and to escape during action, a slight loss of weight was to be expected.

Lavoisier first clearly stated the principle of conservation of mass in 1785 in the form of a law now known as the *law of the conservation of mass*, attributing apparent changes in weight to experimental error. Since his time scientists have been accustomed to regard the law as a sort of axiom, and few experimental researches have been undertaken with the express purpose of testing it; but experiments carried out for other purposes can be cited in its support. Thus the work of the Belgian

chemist Stas (1865) shows that in certain reactions the loss or gain could not have been more than from 2 to 4 parts in 100,000.

In 1906 Landolt published the results of a series of experiments carried out at Berlin in critical test of the law. His general plan was to place the materials which were to act on each other (usually in solution) in the two limbs of a glass vessel of the form represented in Fig. 48. The open ends were then sealed and the vessel weighed. The vessel was then inverted to bring the materials into contact with each other,



FIG. 48

and after the reaction the vessel was again weighed. A large number of such experiments were carried out with every refinement of skill and apparatus, and very slight differences between the two weights were detected. These were never more than a few hundredths of a milligram in a total weight of 100 grams, that is, about 1 part in 10,000,000. It is questionable whether these slight differences exceed the unavoidable experimental error. Certainly we may state the *law of conservation of mass* in the following form: *Within the limits of experimental*

*accuracy no change in the total mass of matter can be detected as a result of any transformation which the matter may undergo.*

2. *The law of definite composition.* The common experiences of the earlier chemists led them to believe that the composition of a pure compound is always the same, though relatively little importance was attached to this belief. The question as to whether this is really so or not became an important issue in the years 1802-1808, as a result of the views of a distinguished Frenchman, Berthollet. On theoretical grounds Berthollet was led to believe that the composition of a substance is somewhat variable, being dependent on the relative quantities of the several materials present at the time of its formation. For example, experiment showed that the composition of iron sulfide is, at least approximately, 63.55 per cent iron and 36.45 per

cent sulfur. Berthollet thought that such figures are only approximate—that when an excess of sulfur is heated with iron a larger percentage of sulfur is present in the product.

These views were strongly opposed by a fellow countryman, Proust, who was professor of chemistry at Madrid during most of the controversy. Proust maintained that *the composition of a pure compound is perfectly definite*, and that when two elements form more than one compound, each has its own exact composition, there being no intermediate gradations. He maintained that apparent variability is due to lack of purity in the compound. Proust's experimental work was very accurate for his time, but his analyses were subject to errors of from 1 to 2 per cent. The advance in experimental exactness has steadily demonstrated the correctness of Proust's conclusions. In 1860 and again in 1866 the Belgian chemist Stas undertook elaborate researches in a critical study of the law of definite composition, his analyses being trustworthy in some instances to within about 1 part in 50,000. Within these limits he showed that the law holds rigidly. In our own time the work of the American chemist Theodore Richards, in a connection to be mentioned a little later, has demonstrated the accuracy of the law within still narrower limits. Within the limits of modern methods of analysis, then, we may state the *law of definite composition*: *The composition of a pure compound is always precisely the same.*

3. *The law of multiple proportion.* Proust investigated the composition of several pairs of compounds formed from the same two elements, and the following table illustrates his results:

COMPOUND	TIN	OXYGEN	COMPOUND	COPPER	OXYGEN
Stannic oxide . . .	78.77%	21.23%	Cupric oxide . . .	79.90%	20.10%
Stannous oxide . . .	88.12%	11.87%	Cuprous oxide . . .	88.82%	11.18%

Proust made no comment on the relation between the ratios of oxygen to metal in the two cases, and his figures suggest none. Three investigators,—Dalton, an English school-teacher (1805),

Wollaston, his fellow countryman (1808), and Berzelius, a Swede (1811),—quite independently of each other, observed a striking relationship in such cases, which has come to be known as *Dalton's law of multiple proportion*, since Dalton first formulated it and was very active in seeking proofs of its validity. He showed that if the composition in such cases is stated *not in per centages but in the weights of one element combined with a fixed weight of the other, then these weights are in the ratio of integer numbers.*

For example, Dalton showed that in nitrous oxide 1 part of oxygen is combined with 1.648 parts of nitrogen, while in nitric oxide 1 part of oxygen is combined with 0.798 part of nitrogen. The ratio of the two weights of nitrogen is therefore 1.648 : 0.798 or 2.06 : 1; that is, 2 : 1 within the limits of error. In the case of two of the hydrides of carbon (marsh gas and ethylene) Dalton found that the ratios of carbon to hydrogen are respectively 4.3 carbon : 2 hydrogen and 4.3 carbon : 1 hydrogen. He also recalculated some of Proust's results, showing that they supported his generalization, though the deviations are as much as 5 per cent.

The results obtained by Berzelius in quite a large number of cases showed the generalization to be true to within possibly 0.3 per cent. In more recent times no definite tests of the law have been undertaken, but analyses of compounds, made with great care for other purposes, have been recalculated to test its accuracy, and within the unavoidable errors of analysis it has been found to be a precise statement of the facts. The composition of the two compounds, water and hydrogen dioxide, affords a good illustration of this law (p. 86). *The law of multiple proportion* may be conveniently stated in the following way: *When two elements, A and B, form more than one compound, the weights of the element A, which combine with a fixed weight of the element B, stand in the ratio of small integers to each other. The most usual ratios are 1 : 1, 1 : 2, 1 : 3, 2 : 3, and 2 : 5.*

4. *The law of combining weights.* A study of the ratios by weight in which various elements combine with each other to form compounds has brought to light a very striking and

unexpected peculiarity. A few examples will suffice to make clear the character of this very important peculiarity.

*Example 1.* Magnesium, calcium, copper, and sulfur are all familiar elements that combine with oxygen to form oxides. Accurate experiment has shown that by weight they combine with oxygen as follows:

1 g. of oxygen combines with 1.52 g. of magnesium to form magnesium oxide

1 g. of oxygen combines with 2.50 g. of calcium to form calcium oxide

1 g. of oxygen combines with 3.97 g. of copper to form copper oxide

1 g. of oxygen combines with 1.00 g. of sulfur to form sulfur oxide

These figures are simply experimental facts that are in no way surprising or suggestive.

Let us now see in what ratio these four elements combine with *some other element*, say chlorine. But instead of selecting 1 g. of chlorine as the standard for comparison, let us see *what weight of chlorine combines with that weight of the four elements which has been found to combine with 1 g. of oxygen*:

1.52 g. of magnesium combines with 4.42 g. of chlorine

2.50 g. of calcium combines with 4.43 g. of chlorine

3.97 g. of copper combines with 4.43 g. of chlorine

1.00 g. of sulfur combines with 1.108 g. of chlorine

These results are certainly very surprising. In the case of the first three elements the *figures which state the weights of the elements that combine with a fixed weight of oxygen (1 g.) also state the weights that combine with a fixed weight of chlorine (4.43 g.)*. In the case of sulfur the weight is different, but it is *exactly* one fourth of the weight required by the other three elements.

*Example 2.*

1 g. of hydrogen combines with 7.94 g. of oxygen (water)

1 g. of hydrogen combines with 15.90 g. of sulfur

1 g. of hydrogen combines with 19.88 g. of calcium

But 15.90 g. of sulfur combines with 19.88 g. of calcium

15.90 g. of sulfur combines with 15.88 g. of oxygen ( $2 \times 7.94$ )

A study of thousands of examples of combination among elements has shown that relations similar to these are always found.

*Each element has a characteristic weight by which it enters into combination, either in proportion to the weight itself or to some integer multiple of this weight. This weight is called its combining weight. We can sum up these facts in the compact statement called the law of combining weights: To each element may be assigned an experimental number which in itself, or when multiplied by some small integer, expresses the weight by which the element*

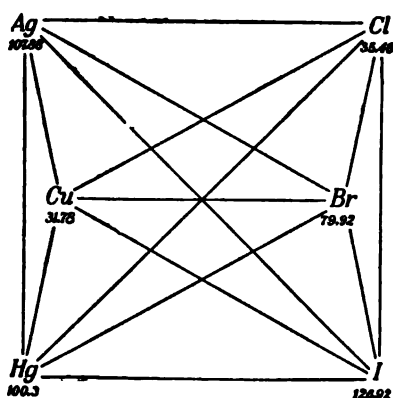


FIG. 49

*enters into combination with other elements.*

*Illustration of the law of combining weights.* The law of combining weights may be graphically illustrated in the diagram (Fig. 49), which gives the symbols of six elements, together with their combining weights as determined by experiment. By following the line connecting any two of these elements we

may see at a glance the ratio by weight in which they combine. Thus 107.88 g. of silver combines with 35.46 g. of chlorine, with 79.92 g. of bromine, and with 126.92 g. of iodine. Similarly, 100.3 g. of mercury combines with 79.92 g. of bromine, and 35.46 g. of chlorine combines with 126.92 g. of iodine. Sometimes an element acts upon a compound in such a way as to displace one of the elements of the compound. Thus copper will displace the silver from silver nitrate, and this takes place in such a way that 31.78 g. of copper displaces 107.88 g. of silver.

**History of the law of combining weights.** This law, which was formerly called the law of reciprocal proportion, was formulated by the German chemist Richter as the outcome of his researches between the years 1792 and 1799. He was of a mathematical turn of mind, and was interested in studying the numerical relations between the weights of combining substances. Most of his studies were concerned with those classes of substances known as acids and bases, which act readily upon each other.

Richter's work did not have any considerable influence upon his contemporaries, owing to a number of causes. His language was obscure and his ideas were expressed partly in terms of the old phlogiston conception and partly in accord with the newer oxygen ideas, and so found favor with the adherents of neither theory. He was led away from the really important part of his work by an endeavor to show that the ratios between the combining numbers of the bases are in arithmetical progression, while those of the acids are in geometrical — which is not true at all.

Richter's ideas were rediscovered and extended by other workers, notably by Berzelius in 1811. It was found that not only to acids and bases but to every substance a number can be assigned which indicates its relative value by weight in chemical reactions. Evidently it would be a very great task to determine by direct experiment the combining number of each known compound, but by applying Richter's ideas to the elements the matter was very greatly simplified.

## II. The determination of the combining weights of the elements.

Since the combining weight of an element is a true constant of nature, it is of the utmost importance that each one should be determined with the greatest possible precision.

1. *The basis for the determination of combining weights.* The problem is apparently a simple one. We must select some one element as a standard and determine what weight of every other element will combine with some fixed weight of this standard. Any element might be taken as the standard, and various choices have been made at different times. Convenience is the chief guide, and this has finally fixed upon oxygen as the choice. Any value might be assigned to oxygen, since the combining numbers are ratio numbers relative to the arbitrary value assigned to the standard. The values 100, 10, 16, and 8 have each been taken as the standard value of oxygen, each suggested by some reason of convenience. It is natural that some integer should be chosen, and 8 is the smallest convenient one. Any smaller value would make the combining weight of hydrogen less than unity, and while this would be no serious matter, it is well to have all values at least as great as unity. *We may therefore define the combining weight of an element as that weight which will combine with 8 g. of oxygen.*

2. *Experimental determination of the combining weight.* The actual experimental determination presents many difficulties when great precision is desired. These are due to the various physical and chemical properties of the substances which must be collected and weighed, the difficulty of obtaining them in an absolutely pure condition, and the inevitable loss in all such operations. Some elements will not combine directly with oxygen, and their combining weights must be calculated. Thus, with bromine we may determine the ratio in which bromine combines with silver, then the ratio of silver to oxygen, and from these two values calculate the ratio of bromine to oxygen. Of course, all the errors of the two experimental ratios may accumulate in the calculated one and make it less trustworthy than a direct determination would be.

**Historical.** Beginning with Berzelius, who devoted many years of his life to the determination of combining weights, some of the most illustrious chemists of each generation have exercised their greatest skill on this problem. For many years the work of Stas, which appeared largely between the years 1860 and 1870, and which included the determination of the combining weights of about a dozen of the most common elements, has been regarded as a model of accuracy. Some of his combining weights are certainly correct to within a few hundredths of one per cent. In 1895 the American chemist Morley published the results of years of labor on the combining ratio between oxygen and hydrogen, the values being trustworthy to one or two units in the third decimal place. At the present time much work is being done along this line, as the combining weights of many of the elements are not accurately known, and there are few which cannot be more carefully determined. Theodore Richards is a leader in this work. He has redetermined the combining weights of a large number of the more common elements with a degree of accuracy never before attained in any considerable series of elements, and has shown that even the work of Stas requires revision in view of the greatly improved methods of research now available.

3. *Atomic weights.* For certain theoretical reasons shortly to be explained, some integer multiple of the combining weight is more frequently employed than the latter weight itself. These multiples are called the *atomic weights*, and the table in Appendix B gives a list of them. The fact that many are

multiples of the combining weights in no way changes their experimental character or modifies their fundamental meaning, for we have seen that the law of multiple proportion states that a multiple of the simplest combining weight will often be necessary to express the composition of a substance. The atomic weights are merely those multiples which, for various reasons, afford the greatest convenience and lead to the most concordant results.

III. The use of atomic weights in expressing facts. The fact that each element has a distinct value of its own in chemical reactions, and that this value can be experimentally determined, suggests a number of convenient applications of the atomic weights in describing chemical changes. Some of these applications will now be considered.

1. *Symbols.* In the table of atomic weights just referred to it will be noted that the name of each element is followed by an abbreviation. This is called its *symbol*. Many of these symbols are abbreviations of the old Latin names and bear no relation to the current English names. Thus, sodium is designated as Na = natrium; antimony, as Sb = stibium; W stands for tungsten, the German name for which is wolfram.

*Symbol weights.* Not only does a symbol stand for a certain element, but it also represents a *definite weight of it*, namely, a weight proportional to its atomic weight. If, as is usually the case, we employ the gram as our standard of weight, then the symbol Na indicates 23 g. of sodium; Sb, 120.2 g. of antimony. Such a weight, expressed in grams, is called the *symbol weight* of an element.

2. *Formulas.* In expressing the composition of a compound we might ignore entirely the weights for which we have agreed to allow the symbols to stand, and use the symbols merely to indicate the elements present in the compound, together with the percentage of each, thus: Fe, 63.52 per cent; S, 36.48 per cent. Obviously this system would be very awkward. It is much more concise and convenient to express composition by giving the *ratio*

of the *symbol weights* of the elements constituting the compound. If we adopt this plan, the united symbols FeS will represent a compound in which iron and sulfur are combined in the ratio of 1 symbol weight of iron to 1 symbol weight of sulfur, namely, 55.84 g. of iron to 32.06 g. of sulfur, making a total of 87.90 g. of iron sulfide.

That these figures state the same composition as the percentage figures first given will be evident from the proportions:

$$87.90 : 100 = 55.84 : x \quad \text{Whence } x = 63.52\% \text{ iron}$$

$$87.90 : 100 = 32.06 : x \quad \text{Whence } x = 36.48\% \text{ sulfur}$$

To convert the percentage figures into symbol figures we need only divide the percentage of each element by its symbol weight to get the *ratio* of symbol weights, thus:

$$63.52 \div 55.84 = 1.137; \quad 36.48 \div 32.06 = 1.137$$

The *ratio* of symbol weights is therefore 1.137:1.137 or 1:1. We can therefore express the composition by the united symbols FeS. Symbols united in this way are called *formulas*. FeS is the formula of iron sulfide, and  $\text{Al}_2\text{O}_3$  is the formula of aluminium oxide.

**Formula weights.** Since each symbol in the formula of a compound represents a definite weight of an *element*, it is evident that the formula itself must represent a definite weight of the *compound*. This weight is equal to the sum of the symbol weights in the formula and is called the *formula weight* of the compound. Thus the formula weight of iron sulfide equals  $55.84 + 32.06 = 87.90$  g.

3. *The calculation of formulas from percentages.* The results of the analysis of a new compound are usually first expressed in percentages. One example of the method of calculating the formula from percentage figures has already been given. A few more examples will be instructive.

**Example 1.** Suppose that an analysis of a certain substance shows it to contain 31.91 per cent K, 28.93 per cent Cl, and

**39.16** per cent O. If each of these percentages is divided in turn by the symbol weight of the element it represents, we shall have *the ratio of the symbol weight of each element present in 100 parts of the compound*:

$$\begin{aligned} 31.91 \div 39.10 &= 0.8161; & 28.93 \div 35.46 &= 0.8159; \\ 39.16 \div 16 &= 2.447 \end{aligned}$$

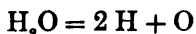
Let us now express the ratio 0.8161 : 0.8159 : 2.447 in terms of integers. To do this we divide all three numbers by the smallest one and obtain the ratio 1 : 1 : 3. The three elements are therefore present in the compound in the ratio of 1 symbol weight of K, 1 symbol weight of Cl, and 3 symbol weights of O. The formula of the compound is therefore  $\text{KClO}_3$ . Since analyses are always slightly inaccurate, the integer ratios will in general differ slightly from true integers, but the values will be so close as to leave no doubt as to the integer in question. The formula  $\text{KClO}_3$  represents the ratio by weight of the three elements as 39.1 : 35.46 : 48 in a total of 122.56, whereas percentages represent it as 31.91 : 28.93 : 39.16 in a total of 100. It will be seen that the ratios are identical.

*Example 2.* We have seen that water is composed of 11.19 per cent of hydrogen and 88.81 per cent of oxygen:

$$11.19 \div 1.008 = 11.10; \quad 88.81 \div 16 = 5.55$$

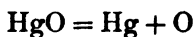
The numbers 11.10 and 5.5 are in the same ratio as are the number of symbol weights of hydrogen and oxygen in water. This ratio is 2 : 1; therefore the formula of water is  $\text{H}_2\text{O}$ .

4. *Equations.* Not only may the composition of compounds be represented by formulas, but the changes taking place in chemical reactions may be represented in the form of equations. For example, the electric current decomposes water into hydrogen and oxygen. This may be represented by the equation

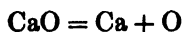


To complete the proof that this equation really represents the whole truth we should have to prove that nothing but hydrogen

and oxygen is formed in the reaction, and that 18.016 g. of water gives 2.016 g. of hydrogen and 16 g. of oxygen, as required by the equation. It will thus be seen that an equation is not merely algebraic but is a summary of experimental fact as well. The equation



represents the change which takes place when mercuric oxide is heated, as shown by experiment. The similar equation



is just as true as an algebraic equation, but it is not true chemically, since calcium oxide cannot be decomposed in this way.

To emphasize the fact that these equations are much more than algebraic statements, chemists make use of an arrow ( $\longrightarrow$ ) in place of the mark of equality, and we shall use this symbol in all future equations.

**5. Representation of energy changes.** We have seen in Chapter I that the changes in energy during a chemical reaction usually result in the liberation or absorption of heat. It is now easy to adopt a system of expressing these energy changes in exact terms. We can add to our chemical equation the number of heat units evolved or absorbed when the weight of material indicated in the equation undergoes reaction. Thus the equation



means that when 32.06 g. of sulfur is burned in oxygen, forming 64.06 g. of oxide of sulfur, 71,080 cal. of heat are set free. The equation

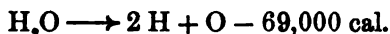


means that when 1.008 g. of hydrogen combines with 126.92 g. of iodine (in solid form), forming 127.928 g. of hydrogen iodide, 6036 cal. of heat are absorbed and must be supplied from without to maintain the temperature.

Finally, it must be noted that these equations do not in any way describe the conditions under which the reaction takes place. The equation



affords no indication that the reaction will not start at ordinary temperatures, though the large quantity of heat evolved suggests that, when once started, it will go on of itself. The equation



does not tell us how water may be decomposed, but merely that in decomposition 18.016 g. will give 2.016 g. of hydrogen and 16 g. of oxygen, and that a great deal of energy (equal to 69,000 cal.) is absorbed in the reaction. Experiment shows that this is best supplied not as heat but in the form of electrical energy.

**IV. The atomic theory.** The four laws explained at length in the earlier pages of this chapter describe the chief characteristics of all chemical action so far as matter is concerned. They state such striking peculiarities that the mind instinctively seeks a theory which will coördinate these facts, affording a mechanical picture of chemical action in harmony with them. The theory accepted for over one hundred years is known as the *atomic theory*, and its essential features were devised by Dalton, who, as we have seen, first announced the law of multiple proportion.

**The essential features of the atomic theory.** The main features of the atomic theory in its present form, together with the experimental reasons for adopting them, may be very briefly stated.

1. It is assumed that every weighable quantity of an elementary substance is made up of a very great number of unit bodies which Dalton named atoms.

2. Since experiment shows that there is no change in mass when two substances act upon each other, it must be true that the masses of the individual atoms of which these substances are composed undergo no change during the action.

3. Experiment also shows that the composition of a given compound is always the same. The simplest way to fit this fact into our theory is to assume that the atoms of each element all have the same mass, while those of different elements have different masses; and that when one element combines with another, the combination takes place between a definite number of each

kind of atoms. It will be seen that if these assumptions should be true, a given compound would of necessity have a perfectly definite composition.

4. The law of multiple proportions reminds us that two elements may combine in more than one ratio to form entirely different compounds, each with its own unchanging composition. The picture we are forming can easily provide for this peculiarity if we assume that the two kinds of atoms can unite in different ratios. For example, if one atom of  $A$  unites with one of  $B$  under one set of conditions, but with two of  $B$  under other conditions, then we shall have the two compounds  $AB$  and  $AB_2$ . The masses of  $B$  in these two, combined with a fixed mass of  $A$ , would then be in the ratio 1:2, which is in complete accord with the law.

5. The law of combining weights tells us that to each element can be assigned a number which expresses its combining value. If we assume that each kind of atom has its own peculiar mass, and that the atoms always combine with each other in definite numbers, then these combining numbers indicate *the relative masses of the atoms themselves*. The fact that an element may have two combining numbers, one an integer multiple of the other, is provided for by the supposition that the atoms are able to combine in several different ratios.

**Summary.** The picture of the make-up of matter and the nature of chemical action which the atomic theory presents may be summed up briefly as follows: *All matter is made up of minute bodies called atoms. The atoms of each element are all alike in mass, but those of different elements have different masses. When elements act upon each other, the action takes place between the different kinds of atoms and in definite numerical ratios.*

**Further explanations.** To prevent misconceptions some further explanations and cautions are desirable.

The size of the atoms. Dalton had no idea as to the size of these atoms, but modern science has thrown much light upon the question. For example, we can measure the thickness of

a soap-bubble film, and this must be *at least* as great as the diameter of a single atom. This measurement gives us an upper limit for the diameter of the atoms in the film. Some intensely colored dyes give a perceptible color to each cubic centimeter of water when 1 g. is dissolved in 100,000,000 cc. of water. This gives us an upper limit by weight, evidently far above the real limit, for each portion of the 1 cc. is colored.

From measurements of this kind Lord Kelvin has calculated that it would take 4,000,000 hydrogen atoms, placed side by side, to make a row 1 mm. long, and that if a drop of water were magnified to the size of the world, the atoms would then be somewhere between small shot and a baseball in size. Whitney has calculated that if the molecules in a glass of water were each to be changed into a grain of sea sand, the resulting sand would cover all the United States to a depth of 100 ft.

**The changeability of atoms.** It should be noted that it is not a part of the theory that there are no conditions under which atoms might be changed in mass — become transformed into other atoms or converted into fragments. It merely assumes that such changes are not a characteristic of chemical action. We shall see later that there is good reason for thinking that some kinds of atoms do undergo transformations which change their mass and character.

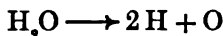
**The different masses of different kinds of atoms.** Experimentally no two elements have been found to have exactly the same combining weight as may be seen from an inspection of the table in the Appendix, though nickel (58.68) and cobalt (58.97) approach each other very closely. Therefore we assume that each kind of atom has its own peculiar mass. It is quite conceivable, however, that the atoms of two elements should have exactly the same mass, the difference between them lying in other properties, such as energy content.

**Molecules and atoms.** In developing his atomic theory Dalton made no distinction between elements and compounds, each being regarded as composed of atoms. Evidently the smallest particle

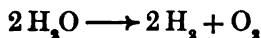
of a compound must be made up of at least two kinds of atoms, while the smallest particle of an element, like oxygen, might consist either of individual atoms or of small groups of similar atoms combined like the atoms in a compound particle. In time it was found convenient to make a distinction. The term "*molecule*" is now applied to the smallest unit either of a compound or of an element, which, taken in large aggregations, makes up the bodies we deal with, and into which substances can be divided without chemical decomposition. The term "*atom*" is applied to the smallest unit of an element into which we can decompose molecules.

**Atomic weights and molecular weights.** Since the mass of each kind of atom is always the same, it will be seen that some one set of numbers may be chosen which will represent the relative masses of each of the atoms, and that these numbers will be either the combining numbers themselves or some integer multiple of them. The choice of the real atomic ratio number from among the possible combining numbers has presented great difficulties historically, but we now have sound principles for our guidance. These will be developed in a subsequent chapter. For the present we may assume that the numbers in the atomic table (Appendix B) do represent the real atomic ratios, and are therefore properly called atomic weights. When we make use of the atomic theory, therefore, in expressing chemical facts, the symbol of an element represents an atom, while a formula represents a molecule.

Thus we have good reason for thinking that the gases we call oxygen and hydrogen are made up of molecules having the compositions represented by the formulas  $O_2$  and  $H_2$ . When water is decomposed, the first action seems to be the parting of the water molecules into the two kinds of atoms:



These at once combine to form molecules of the two gases, so that the final condition is represented by the equation



With mercury and other metals, when in the form of vapor, the atoms do not appear to form molecules, so that mercury vapor is represented by the formula  $\text{Hg}$ , not  $\text{Hg}_2$ .

**Gram-atomic and gram-molecular weights.** In accordance with the usage just explained the term *gram-atomic weight* is often employed instead of *symbol weight*, and *gram-molecular weight*, or *molar weight*, instead of *formula weight*. Both really mean the same thing, namely, as many grams of the element or compound as there are units in its symbol or formula.

**Molecular formulas.** If, as is the custom, we make use of formulas to represent not only the composition of a compound but also the number of atoms in its molecule, it may easily happen that the simplest formula, calculated according to the method already described (p. 114), will not fulfill these conditions. Thus the simplest formula correctly representing the composition of hydrogen peroxide is  $\text{HO}$ ; but there is good reason for believing that the molecules of the compound really consist of two atoms of hydrogen and two of oxygen, giving the formula  $\text{H}_2\text{O}_2$ . It has been found possible to devise methods which give us the true molecular formulas (or molecular weights) of most compounds other than solids, and these will be described in a subsequent chapter.

**The atomic conception no longer a theory.** Until comparatively recent years the atomic theory was very properly regarded as having much the same value as any other good theory. It afforded us a picture that was very helpful in giving a meaning to the four laws of chemical combination, and it suggested many lines of experimental work. This work has been so fruitful and our knowledge has increased to such an extent that we now have no doubt that atoms are real things. We even feel quite sure that each kind of atom has a structure of its own, and we are making rapid progress in forming definite pictures of these various structures. What was formerly regarded as a good theory has become a truth, and we should now speak of the atomic reality rather than of the atomic theory.

## QUESTIONS

1. Would you say of the two compounds  $\text{BaO}$  and  $\text{BaO}_2$  that the second contains twice as much oxygen as the first?
2. Tell whether the following is a correct statement of the law of multiple proportion: If two elements  $A$  and  $B$  combine to form two different compounds, the *percentages* of  $A$  in the two will be in the ratio of integer numbers.
3. Tell all that is indicated to you by the formula  $\text{H}_2\text{O}$ ; by the formula  $\text{KClO}_4$ ; by the formula  $\text{H}_2\text{SO}_4$ .
4. (a) In what respects does a chemical equation differ from an algebraic equation? (b) In what respects are they similar?
5. Apart from the reference in this chapter, in what other connection have we met with the name of the chemist Berzelius?
6. Distinguish between combining weight, atomic weight, molecular weight.

## PROBLEMS

1. Using the data in the table on page 107 show that in the two oxides of copper and also in the two oxides of tin the weights of oxygen are in multiple proportion.
2. Copper combines with chlorine, with bromine, and with iodine. From the diagram on page 110 calculate the percentage by weight of each of the compounds formed.
3. If chlorine had been selected as standard for atomic weights with a weight of 100, then from the diagram on page 110 calculate the atomic weight of silver and of copper.
4. Calculate the percentage composition of the compound having the formula  $\text{CuSO}_4$ . Refer to the table in the Appendix for the atomic weights.
5. A compound was found to have the following composition:  $\text{Ca} = 26.3\%$ ;  $\text{S} = 42.1\%$ ;  $\text{O} = 31.6\%$ . Calculate its formula.
6. How much heat is liberated by the combustion of 500 g. of sulfur?

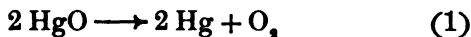
## CHAPTER VIII

### EQUATIONS AND CALCULATIONS; VALENCE

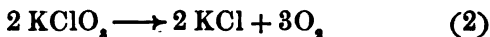
**Equations of reactions so far studied.** In the chapters on Oxygen, Hydrogen, and Water, reactions were described which must now be reviewed and put into the form of definite equations. It will be found profitable to turn back to the description and associate the reactions with the equations as they are now given.

#### 1. *The preparation of oxygen.*

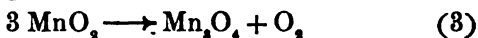
Decomposition of mercuric oxide:



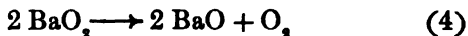
Decomposition of potassium chlorate:



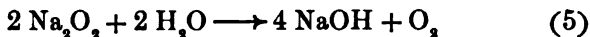
Decomposition of manganese dioxide:



Decomposition of barium peroxide:



Action of sodium peroxide on water:

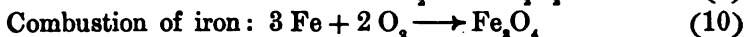
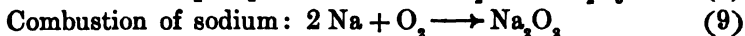
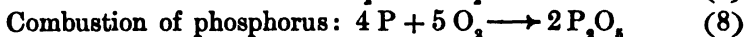
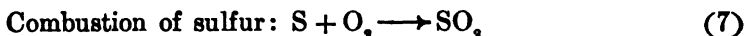


Electrolysis of water:  $2 \text{H}_2\text{O} \longrightarrow 2 \text{H}_2 + \text{O}_2$  (6)

It must be kept in mind constantly that such equations are merely a very condensed way of stating quantitative chemical facts that have been found out by experiments. In reading the equation the full statement should be recalled. Thus equation (2) is a statement that under appropriate conditions two formula weights of potassium chlorate give two formula weights of potassium chloride and three formula weights (six symbol

weights) of oxygen. In terms of atomic relations the statement is that two molecules of the chlorate give two of the chloride and three of oxygen.

### 2. *The action of oxygen upon elements.*



It will be noted that these four elements are represented as though their molecules consisted of but a single atom. This is probably not the case, but we have no satisfactory way of determining how many atoms are present in the molecule of any *solid* substance, and in the absence of other information we represent it by the simplest possible formula. On the other hand, the solid compound sodium peroxide ( $\text{Na}_2\text{O}_2$ ) might be represented by the formula  $\text{NaO}$  just as well, but the double formula more satisfactorily expresses many of its reactions.

### 3. *The preparation of hydrogen.*



Decomposition of water by sodium:



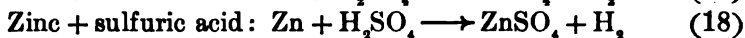
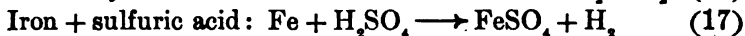
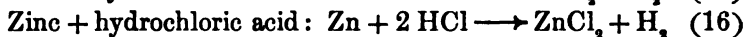
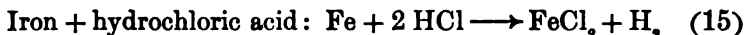
Decomposition of water by magnesium:



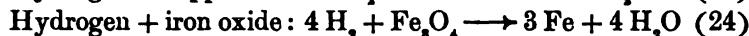
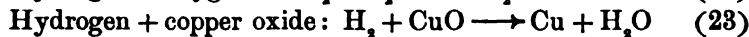
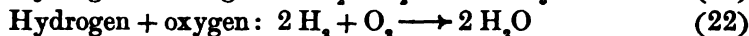
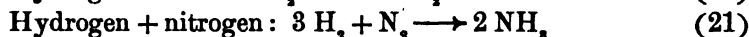
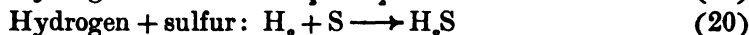
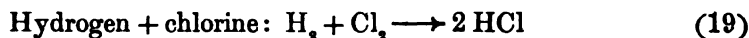
Decomposition of water by iron:



Action of acids on metals.



The formula  $\text{Mg}(\text{OH})_2$  in equation (13) is merely a more convenient way of writing  $\text{MgO}_2\text{H}_2$ , and represents the same thing.

4. *The action of hydrogen with other substances.*

5. *Water of crystallization.* Experiment has shown that the water with which certain compounds unite to form hydrates (p. 78) always bears a definite ratio by weight to the compound, and the resulting hydrate therefore has a definite formula. Thus the blue hydrate of copper sulfate, when heated, loses 36.07 per cent of its weight as water, which corresponds to five formula weights of water to one of the sulfate. Copper sulfate has the formula  $\text{CuSO}_4$ , so that the composition of the hydrate may be expressed by the formula  $\text{CuSO}_4\text{H}_{10}$ . It is customary, however, to retain the formulas of the two original compounds, indicating the hydrate by the formula  $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ . When this hydrate is heated, the hydrogen and oxygen are given off as water, leaving the copper sulfate:



It must be understood that this usage is for convenience in recognizing that the compound is a hydrate of copper sulfate, and is not intended to convey the impression that water as such exists in the hydrate.

6. *The preparation of hydrogen peroxide.*

Barium peroxide + sulfuric acid:



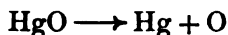
Barium peroxide + phosphoric acid:



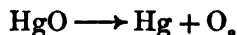
**Balancing equations.** A chemical equation should be regarded as a very compact way of stating many facts in what may be

called a chemist's peculiar shorthand language, and it requires a good deal of practice to use the symbols of this language with ease. A few examples will be of assistance.

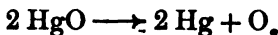
**Example 1.** The *qualitative* facts expressed in equation (1) are that under favorable circumstances (high temperature) mercuric oxide decomposes into mercury and oxygen gas. Careful preliminary experiment has shown that mercuric oxide has the formula  $\text{HgO}$ . As a first trial for an equation we may now write



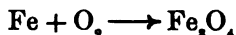
But we have methods that convince us that the formula of oxygen gas is  $\text{O}_2$ , whereas we have no evidence that the atoms of mercury unite to form molecules. As a second trial we therefore write



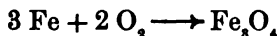
But to supply the two atoms of oxygen for  $\text{O}_2$ , we must take two molecules of  $\text{HgO}$ , and this will give us 2 Hg as well as  $\text{O}_2$ . So finally we have



**Example 2.** The experimental facts we have to know before we can write equation (10) are these: When oxygen gas ( $\text{O}_2$ ) is passed over hot iron an oxide of iron is formed having the formula  $\text{Fe}_3\text{O}_4$ . We can then at once write



But our equation must balance. In other words, it must show the same number of atoms of each kind on each side of the arrow; otherwise it would not be in accord with the law of conservation of mass. To get  $\text{Fe}_3$  we must write 3 Fe on the left side of the equation, and to get  $\text{O}_4$  we must write 2  $\text{O}_2$ . We then have



**Summary.** First write down the formulas of the elements or compounds or both entering into the reaction on one side, and the formulas of all products formed, on the other side of an equation. Then, by trial, place coefficients before the formulas to make the equation balance.

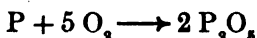
**Example** (equation 8).

First step:



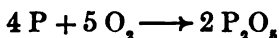
But  $\text{O}_5$  in  $\text{P}_2\text{O}_5$  is supplied by  $\text{O}_2$ , and we must multiply each one by a coefficient that will bring the two to the same value.

Second step:



This requires us to supply 4 atoms of phosphorus.

Third step:



**Types of reactions.** A study of the reactions so far considered shows that they may be classified into four distinct types, and we shall find that almost all of the reactions which we shall meet can be assigned to one of these four.

1. **Direct union.** Two elements (or compounds) may unite to form a compound. This is illustrated by the combustion of substances in oxygen and the action of hydrogen upon different elements. (Equations (7) to (10) and (19) to (22).)

2. **Decomposition.** A compound may decompose into other compounds or elements, as is the case when mercuric oxide, or potassium chlorate, or manganese dioxide is heated (equations (1) to (4)).

3. **Substitution.** One element may take the place of another in a compound, the substituted element being set free. This is the case when the metals zinc and iron act upon hydrochloric or sulfuric acids, liberating hydrogen (equations (15) to (18)). Equations (12) to (14) are also illustrations of substitution.

4. **Double decomposition.** This is probably the most common type of reaction and consists in the interchange of two elements present in two different compounds, thus resulting in the formation of two new compounds. It is illustrated in equations (26) and (27), which represent the reaction taking place in the preparation of hydrogen peroxide. In these reactions it will be seen that the barium of barium peroxide and the hydrogen of the acids change places, forming two new compounds.

**Valence of the atoms.** A careful inspection of the formulas of the compounds in the foregoing equations can hardly fail to result in an interesting observation. The atoms evidently differ among themselves in *respect to the number of other atoms with which they can combine*. Confining our attention to those formulas that contain only two kinds of atoms, we see that an atom of hydrogen, chlorine, or potassium seems unable to combine with *more than one other atom*. This is shown in the formulas  $\text{HCl}$  and  $\text{KCl}$ . On the other hand, an atom of oxygen or of sulfur can combine with two of hydrogen ( $\text{H}_2\text{O}$ ,  $\text{H}_2\text{S}$ ), while an atom of iron or of zinc can combine with two of chlorine ( $\text{FeCl}_2$ ,  $\text{ZnCl}_2$ ). It will be noticed also that when sodium ( $\text{Na}$ ) acts upon water each atom *displaces* only one of hydrogen; while when iron or zinc acts upon either hydrochloric acid or sulfuric acid each atom displaces two of hydrogen.

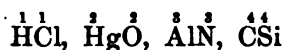
These observations bring into view a fundamental property of the atoms called *valence*. *The valence of an atom is that property which determines how many atoms of another kind it can hold in combination or displace in a reaction.*

**Standard of valence.** Since the atoms of neither hydrogen nor chlorine combine with more than one atom of another kind (to form a compound which contains only two kinds of atoms), they are called *univalent* atoms, and serve as a standard for determining the valence of other atoms. Oxygen, sulfur, iron, and zinc, whose atoms combine with two of hydrogen or of chlorine, are called *bivalent*. There are other elements whose atoms have still higher valences of three (trivalent), four (quadrivalent), and so on up to a valence of eight.

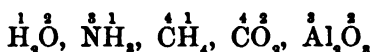
From all that has been said it might be inferred that in the compound  $\text{CuO}$  the atoms both of copper and of oxygen are univalent, because there is one of each in the molecule of copper oxide. But measured by hydrogen, oxygen is bivalent ( $\text{H}_2\text{O}$ ). Consequently copper must be bivalent also. We must always keep in mind that oxygen is bivalent when we deduce the valence of an element from the formula of its oxide.

**Applications of valence.** While it is not possible at this point to take up a complete discussion of the subject of valence, the following general principles will be of service:

(a) If two elements which have the same valence combine to form a compound, they will combine atom for atom, as shown in the following formulas in which the valence of the atom of each element is designated by the figure above the symbol:



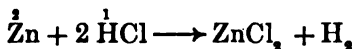
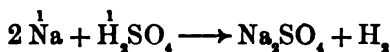
(b) If two elements which have different valences combine to form a compound, then such numbers of atoms of the two elements will combine as will add up an equal number of valences, thus:



Hydrogen is univalent while oxygen is bivalent, as is expressed by the figures over the formula of water. There is 1 atom of oxygen (2 valences); hence there must be a sufficient number of hydrogen atoms to add up 2 valences, namely, 2 atoms.

Again, in the formula for carbon dioxide,  $\text{CO}_2$ , the carbon is quadrivalent. Hence, for each atom of carbon (4 valences) there must be 2 atoms of oxygen (4 valences).

(c) In a reaction in which one element takes the place of another in a compound (see Substitution, p. 127) the exchange must be between such numbers of atoms of the two elements involved as will add up an equal number of valences; for example, 1 atom of a bivalent element will displace 2 atoms of a univalent element, while 2 atoms of a trivalent element (6 valences) will displace 3 atoms of a bivalent element (6 valences):



(d) In reactions of double decomposition (p. 127) the interchange must be between such numbers of atoms of the two

elements as will add up an equal number of valences; thus sodium and hydrogen, each being univalent, will displace each other atom for atom:



With very few exceptions the elements do not have a single fixed valence. Most of them have 2 valences and some have more. Thus mercury forms the compounds  $\text{HgCl}$  and  $\text{HgCl}_2$  in which the mercury is univalent and bivalent, respectively. Similarly, tin forms compounds represented by the formulas  $\text{SnCl}_2$  and  $\text{SnCl}_4$ . Moreover, an element often has one valence for one kind of an element and a different valence for another. Thus sulfur is bivalent in the compound  $\text{H}_2\text{S}$  but quadrivalent in the compound  $\text{SO}_2$ .

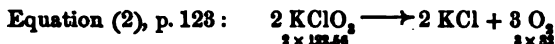
**Difficulties.** While the general idea of valence is of great assistance, yet it must be added that the student will meet with many cases which, at first sight at least, are misleading. Thus, in the formula for hydrogen peroxide,  $\text{H}_2\text{O}_2$ , one would be inclined to say that hydrogen and oxygen have the same valence; while the formula for iron oxide,  $\text{Fe}_3\text{O}_4$ , would indicate that the iron has a valence of  $2\frac{2}{3}$ , which is an absurdity. These cases, however, are not numerous and will be explained in later chapters. The usual valences of the elements will become familiar as we study the formulas of their compounds. They should be learned in this way rather than from tables of valence.

**Chemical calculations.** Equations such as the ones which have just been presented are merely a convenient form in which to record the results of experiment. They represent the composition of substances entering into reaction with each other, and the proportion by weight in which they take part in the reaction; they also represent the weights and compositions of the products formed. When properly verified by experiment they may be employed very conveniently in solving many problems which involve chemical transformations. A few typical examples will now be given, together with the method of solution.

1. What weight of oxygen can be obtained by heating 20 g. of potassium chlorate?

The formula weight (or molecular weight) of potassium chlorate is

$$39.1 + 35.46 + 3 \times 16 = 122.56$$



The equation tells us that the ratio by weight between the chlorate decomposed and the oxygen obtained is always 245.12:96. The quantity obtainable from 20 g. of chlorate may therefore be found from the proportion:

$$\begin{aligned} 245.12:96 &= 20:x \\ x &= 7.83 \text{ g.} \end{aligned}$$

We have already solved problems similar to the above, in connection with Chapter II. They were solved without reference to symbol weights and formula weights. It was necessary, however, to know the percentage of oxygen present in potassium chlorate, and this information was furnished. If we know the symbol weights of the elements and the equation for the preparation of oxygen, it is easy by the above method to solve such problems from these data alone.

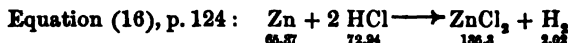
2. What weight of oxygen will be required for the combustion of 25 g. of iron?



The iron stands to the oxygen in the ratio 167.52:64. Consequently

$$\begin{aligned} 167.52:64 &= 25:x \\ x &= 9.55 \text{ g.} \end{aligned}$$

3. What weight of zinc will be required to liberate 10 g. of hydrogen by its action with hydrochloric acid?



Since hydrogen and zinc stand in the ratio 2.02:65.37, therefore

$$\begin{aligned} 2.02:65.37 &= 10:x \\ x &= 323.8 \text{ g. zinc} \end{aligned}$$

4. What weight of zinc chloride ( $\text{ZnCl}_2$ ) will be produced at the same time?

The hydrogen and zinc chloride are formed in the ratio 2.02:136.3; consequently

$$\begin{aligned} 2.02:136.3 &= 10:x \\ x &= 674.7 \end{aligned}$$

5. Some of the common acids are always sold in the form of concentrated solutions, the label on the bottle bearing a statement as to the

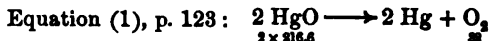
density of the solution and the percentage by weight of acid in it. Thus the concentrated hydrochloric acid of commerce usually has a density of 1.20 and contains 40 per cent of the compound HCl. Let it be required to calculate what *volume* of such a solution will be used in producing 10 g. of hydrogen, as in problem 3. It must be remembered that the volume of a liquid multiplied by its density gives its weight (that is,  $V \times D = Wt$ ), and that of this weight only 40 per cent is the material we are concerned with. The weight of the compound HCl is obtained from the proportion

$$\begin{aligned} 2.02 : 72.94 &= 10 : x \\ x &= 361 \text{ g. HCl} \end{aligned}$$

This is 40 per cent of the *weight* of the solution required, the whole solution weighing  $\frac{361}{40} \times 100 = 902.5$  g. Dividing this by the density of the solution, 1.2 (in other words, by the weight of 1 cc.), we have  $\frac{902.5}{1.2} = 752.08$  cc.

**Problems involving calculations of volume.** It is often required to calculate the volume of a gas which can be obtained in a given reaction when measured under ordinary laboratory conditions, or what *weight* of materials will be required to produce a desired *volume*. Since chemical equations deal with *weights*, not volumes, it is always necessary, as a first step, to determine the weight of the gas, and from this to calculate its volume. Since the weight of a unit volume of a gas varies with every change in temperature and pressure, it would evidently be a great task to tabulate all possible weights for reference. Consequently the tables (such as the one in the Appendix) give merely the weight under standard conditions, and a measured volume of a gas must always be reduced to these conditions before its weight can be calculated.

6. What volume of oxygen, measured under ordinary laboratory conditions (say 750 mm. and 20°), may be obtained by heating 100 g. of mercuric oxide?



$$433.2 : 32 = 100 : x$$

$$x = 7.39 \text{ g. oxygen}$$

1 l. of oxygen (standard) weighs 1.429 g. (see Appendix)

$$7.39 + 1.429 = 5.17 \text{ l. (standard)}$$

To ascertain the volume which this will occupy under laboratory conditions we may employ the equation on page 61:

$$V_s = \frac{P \times V \times 273}{760 \times T}$$

Substituting, we have

$$5.17 = \frac{750 \times V \times 273}{760 \times 293}$$

Solving for  $V$ , the volume under laboratory conditions, we obtain  $V = 5.62$  l.

7. How many grams of potassium chlorate will be required to yield 10 l. of oxygen measured under ordinary laboratory conditions? In this case the volume under standard conditions must be calculated before the weight can be found.

$$V_s = \frac{P \times V \times 273}{760 \times T} = \frac{750 \times 10 \times 273}{760 \times 293} = 9.19 \text{ l. (standard)}$$

$$9.19 \times 1.429 = 13.13 \text{ g. oxygen}$$



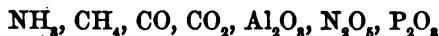
$$96 : 245.12 = 13.13 : x$$

$$x = 33.53 \text{ g. potassium chlorate}$$

It is useful to observe, as a check on such calculations, that in reducing to standard conditions a volume measured under ordinary laboratory conditions, the decrease in volume amounts to about 8 or 10 per cent, with a corresponding increase when the reduction is in the reverse direction. The student should also cultivate the habit of noticing whether his results seem reasonable, since arithmetical errors are easily made in such calculations.

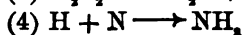
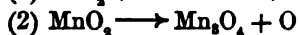
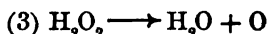
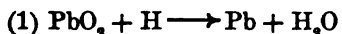
### QUESTIONS

1. Assuming that hydrogen is always univalent and oxygen always bivalent, state the valence of each of the elements in the following compounds:



2. Aluminium and carbon form a compound in which the aluminium is trivalent and carbon quadrivalent. What is its formula?

3. Balance the following incomplete equations:



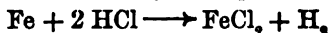
4. Aluminium in contact with hydrochloric acid displaces the hydrogen of the acid, liberating free hydrogen. Complete and balance the following equation:



5. Complete and balance the following equation, representing a reaction in which the hydrogen of the compound  $\text{H}_2\text{S}$  and the antimony (Sb) of the compound  $\text{SbCl}_3$  replace each other:



6. Explain all that is indicated by the equation:



7. Why not write the equation for the decomposition of mercuric oxide as in (1) rather than to just double this as in (2)?



If you were solving a problem involving the decomposition of mercuric oxide, could the simpler equation (1) be used to calculate the relative weights of the reacting substances just as well as equation (2)?

### PROBLEMS

1. (a) What weight of hydrogen can be obtained by acting upon 100 g. of iron with sulfuric acid? (b) What volume will this occupy under standard conditions?

2. What volume would the hydrogen obtained in problem 1 occupy if measured over water in a laboratory at  $20^\circ$  and 740 mm.?

3. (a) What is the volume of hydrogen evolved when 200 g. of sulfuric acid is added to 50 g. of iron in a flask? (b) What products will be left in the flask after the reaction ceased?

4. In the preparation of 100 l. of oxygen by heating potassium chlorate, what weight of potassium chloride is formed?

5. (a) If the yield obtained was 80 per cent of the theoretical yield, what weight of the ordinary hydrogen peroxide of the druggist could you obtain from 200 g. of barium peroxide? (b) What weight of sulfuric acid would be required in the reaction?

6. Which will liberate the more hydrogen from sulfuric acid, 100 g. of iron or 100 g. of zinc?

7. A certain dirigible balloon has a capacity of 30,000 cu. yd. If the hydrogen is generated by the action of steam on iron, what weight of iron is necessary to prepare sufficient hydrogen to inflate the balloon at  $20^\circ$  and 740 mm. (1 yd. = 0.9144 m.)?

## CHAPTER IX

### CARBON ; CARBON DIOXIDE

**Occurrence.** In the free condition carbon is found in nature in several forms. The diamond is practically pure carbon, while hard coal (anthracite) and graphite are largely composed of the free element. Its natural compounds are exceedingly numerous and occur in the form of gases, liquids, and solids. Carbon dioxide (often called carbonic acid gas) is its most familiar gaseous compound. Natural gas and petroleum are composed principally of *hydrocarbons*; that is, of compounds of carbon and hydrogen. The carbonates, especially calcium carbonate (marble and limestone), constitute great strata of rocks and are found in almost every locality. Living organisms, both plant and animal, contain a large percentage of combined carbon, and the number of its compounds which go to make up all the vast variety of animate nature is almost limitless. It is in a sense regarded as the element most closely related to life itself, although it is undoubtedly true that the other elements normally present in the tissues of living organisms all play an essential part in the growth of the organism.

**Forms of carbon.** Carbon occurs in three allotropic forms, two of which are crystalline and the third is amorphous.

**Crystalline forms of carbon.** Two forms of crystalline carbon occur in nature, namely, the diamond and graphite.

**Diamond.** This form of carbon has long been known and highly prized as a gem. Diamonds are found in several localities, especially in South Africa, the East Indies, and Brazil. The crystals belong to the isometric system, although the natural crystals are always more or less imperfect. As commonly found in nature, they are covered with a rough coating. In order to

bring out the brilliancy of the gem, the natural crystal is cut in such a way that the light is most effectively refracted.

A pure diamond is perfectly transparent and colorless, but many are tinted a variety of colors by traces of foreign substances. Usually the colorless forms are the most highly prized, although in some instances the color adds to the value, as in the case of the famous Hope diamond, which has a beautiful blue tint.

The weight of the diamond is expressed in carats. Each carat is equal to about 0.2 g. The word *carat* is derived from a Greek word meaning "the seed, or bean, of the carob, or locust tree." The beans were formerly used in weighing diamonds.

The largest diamond known was found in the Transvaal mines in 1905, and weighed  $3025\frac{1}{4}$  carats. This was known as the Cullinan diamond and was presented to King Edward VII by the Transvaal government. It was subsequently cut into nine large stones and a number of smaller ones. The two largest of these weigh 516.5 and  $309\frac{1}{8}$  carats and are the largest cut diamonds in existence. Other famous diamonds are the Kohinoor ( $106\frac{1}{4}$  carats), the Nizam (277 carats), the Victoria (180 carats), and the Jubilee (289 carats).

**Composition and properties of the diamond.** The density of the diamond is 3.52, and, though brittle, it is one of the hardest of substances. Specimens are often found in nature that are identical, in composition and properties, with the ordinary diamond, except that they are black and therefore valueless as gems. Few chemical reagents have any action upon the diamond, but when heated in pure oxygen or air it blackens and finally burns, forming carbon dioxide. Lavoisier was the first to show that carbon dioxide is formed by the combustion of the diamond in pure oxygen, thus proving that it contains carbon. Later (1814) Sir Humphry Davy showed that carbon dioxide is the sole product of the combustion, and by determining the relation between the weights of the diamond burned and the carbon dioxide produced he proved that the diamond is pure carbon.

**Artificial preparation of diamonds.** Many attempts have been made to produce diamonds artificially. These attempts were unsuccessful until Moissan, in 1893, finally succeeded in producing diamonds identical in every way with the natural gem. The method used by Moissan consisted in dissolving pure carbon in molten iron and quickly cooling the resulting

solution by plunging the crucible containing it into water. Under these conditions a portion of the carbon separated in the form of crystals. The iron was then removed by dissolving it in acids. The largest of the crystals so obtained, however, had a diameter of only 0.5 mm. and were thus too small to have any value as gems.

**Graphite.** This form of carbon is found in large quantities in nature, especially in Ceylon, Siberia, and some localities in the United States, Mexico, and Canada. It is a shining black substance, very soft and greasy to the touch. Its density is about 2.3. It varies somewhat in properties, according to the locality in which it is found. When any form of carbon is heated in an electric furnace to a temperature of about  $3500^{\circ}$ , it rapidly vaporizes, and the vapor always condenses in the form of graphite. This property has led to the production of graphite on a commercial scale.

Graphite is used in the manufacture of crucibles, as a lubricant, and as a protective cover for iron in the form of a paint or polish, such as stove polish. It has long been used in the manufacture of lead pencils, a fact which is indicated by its name, which is derived from a Greek word meaning "to write."

**The commercial production of graphite.** The method of producing graphite commercially was worked out by Acheson, an American scientist. The process consists essentially in heating carbon in large electric furnaces

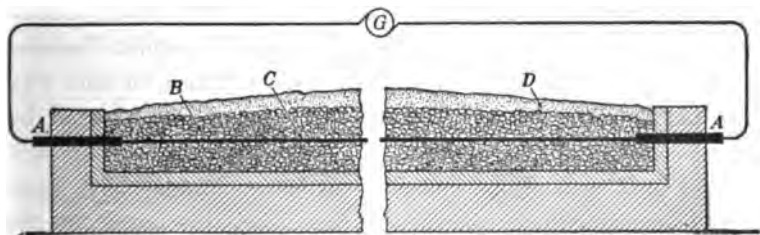


FIG. 50

about 40 ft. in length, a longitudinal section of which is shown in Fig. 50. The electrodes *A, A* are made of graphite. The walls of the furnace are built of some infusible material. The furnace is nearly filled with some form of carbon, such as coarse grains of anthracite coal, *B*. Since anthracite

coal is a poor conductor of electricity, there is placed in the center of the charge a core (*C*) of granulated carbon, connecting the two electrodes, the core serving to conduct the current through the charge. The charge is covered with a mixture of sand and carbon (*D*) or similar materials, which serves to exclude the air. An alternating current (40,000 amperes at 200 volts) is supplied by the generator *G*. Under the influence of the intense heat produced by the current the carbon is changed into the form of graphite. Prepared in this way, the product is uniform in composition and free from grit, and is therefore superior to the natural product for many purposes.

**Amorphous carbon.** Many varieties of amorphous carbon are known. Some of these, as the various forms of coal, are found in nature, while others, such as charcoal and coke, are easily prepared. These forms differ merely in their degree of purity and in their physical condition. They are of the greatest importance, owing to their many uses in the arts and industries.

1. **Pure carbon.** Pure amorphous carbon is best prepared by charring ordinary sugar. This compound has the composition expressed by the formula  $C_{12}H_{22}O_{11}$ . When strongly heated, the oxygen and hydrogen are expelled largely in the form of water, while pure carbon is left. Prepared in this way, carbon is a soft, very bulky, black powder. It was by this method that Moissan obtained the carbon which he used in the preparation of artificial diamonds.

2. **Coal and coke.** Coals of various kinds have been formed from vast accumulations of vegetable matter, which became covered with water and earthy material and were in this way protected from rapid decay. Under the influences exerted by various geological agencies this organic matter was slowly changed into coal. In anthracite coal these changes have gone the farthest, and the carbon in this kind of coal is largely in the free condition. Soft, or bituminous, coals, on the other hand, contain a much larger percentage of combined carbon. When heated strongly out of contact with air, as in the manufacture of coal gas, the carbon compounds undergo complicated changes resulting in the formation of a large number of substances which

are given off in the form of gases and vapors, while the mineral matter and free carbon remain behind and constitute ordinary coke. The process will be discussed more in detail in the chapter dealing with fuel gases.

3. *Charcoal*. This form of carbon has long been used as a fuel and as a reducing agent in obtaining metals from their oxides. It is prepared by heating wood in the absence of air, just as coke is prepared from coal under like conditions. Formerly this process was carried out in a wasteful way by merely covering piles of wood with sod and then igniting the wood. By this process some of the wood is burned, while the remainder is decomposed by the heat, forming charcoal. In heating wood, just as in heating coal, many valuable volatile products are formed. In the preparation of charcoal by the older methods these products are all lost. At present an increasing quantity of charcoal is made by heating the wood in large retorts, and the volatile products are condensed and saved as in the case of coal. Among the products so obtained are *wood alcohol*, *acetic acid*, and *acetone*, as well as a number of less important substances. The mineral constituents of the wood remain in the charcoal. The relative composition of coal, coke, wood, and charcoal is represented approximately by the following analyses of typical samples:

	TOTAL CARBON	HYDRO- GEN	OXYGEN	NITRO- GEN	SULFUR	ASH	TOTAL VOLATILE MATTER
Coal (anthracite) .	82.04%	2.70%	3.50%	0.77%	0.74%	10.25%	5 to 8%
Coal (semi-bituminous) . .	82.71%	4.43%	3.98%	1.33%	0.68%	6.87%	18 to 20%
Coal (bituminous)	78.03%	4.99%	6.11%	1.53%	1.05%	8.29%	30 to 35%
Wood . . . . .	40.00%	7.20%	50.70%	0.80%	traces	1.30%	80 to 90%
Coke . . . . .	89.00%	traces	traces	traces	0.80%	10.20%	traces
Charcoal . . . . .	97.00%	traces	traces	traces	traces	3.00%	traces

**Modern methods for the production of charcoal.** Fig. 51 shows the essential parts of a modern plant for making charcoal. The iron cars *A, A* loaded with from one to three cords of wood are run into the retort *B*,

and the door closed. The retort is then heated slowly for about twenty-four hours, the heat being generated in the fireplace *F, F*. The volatile products escape through the pipes *C, C* and pass through the condensers *D, D*. Here those portions which are liquid at ordinary temperatures (wood alcohol, acetic acid, and acetone) are condensed and flow off through pipes *E, E* to suitable containers, while the gaseous products are led back into the fireplace and burned. After the volatile matter is expelled from the wood, the retort is allowed to cool somewhat, and the cars containing the charcoal are run out of the retort into cooling chambers, their places in the retort being taken by other cars loaded with wood.

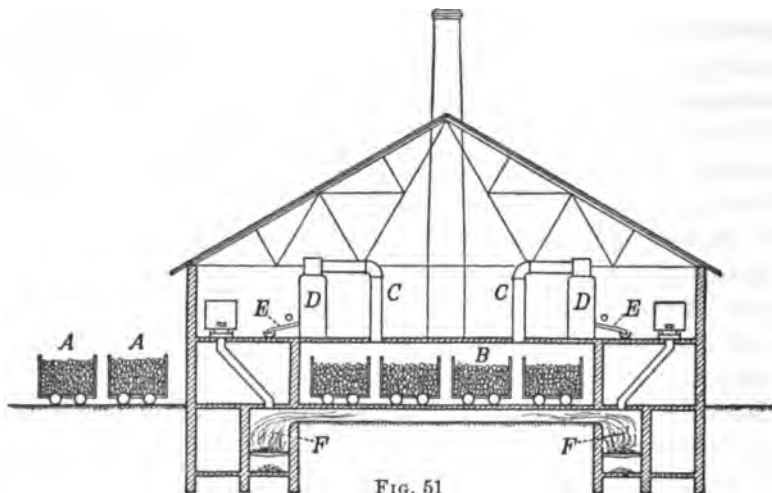


FIG. 51

4. **Boneblack.** This form of carbon is sometimes called *animal charcoal* and is made by heating bones and animal refuse in the absence of air. Bones are composed of about 40 per cent organic matter and 60 per cent mineral matter, chiefly calcium phosphate. When heated in the absence of air the organic matter is decomposed, resulting in the formation of volatile matter and free carbon, which remains, in a finely divided state, scattered through the mineral portion of the bone. The boneblack so obtained consists principally of calcium phosphate with a relatively small percentage of carbon. For some uses it is desirable that the mineral part be removed, and this is done by the action of

hydrochloric acid, which dissolves the calcium phosphate but has no action upon the carbon. For most purposes, however, the presence of the calcium phosphate is not objectionable.

**Bone oil.** The volatile matter formed in the heating of bones condenses to a dark-colored, foul-smelling liquid known as *bone oil*. It is a mixture of a number of compounds, important among which is pyridine ( $C_5H_5N$ ), a compound sometimes added to alcohol to render it unfit for drinking.

**Destructive distillation.** The process of decomposing such substances as coal, wood, and bones by heating them in the absence of air is termed *destructive distillation*. As commonly expressed, coke, charcoal, and boneblack are made by the destructive distillation of coal, wood, and bones, respectively.

5. **Carbonblack; lampblack.** When a gas flame, burning in an amount of air insufficient for complete combustion, is allowed to impinge against a cold surface, such as a revolving iron drum, much of the carbon present in the compounds constituting the gas is not consumed but is deposited on the cold surface. This form of carbon is known as *carbonblack*. It is nearly pure carbon, but still contains some hydrogen compounds. It is used in large quantities in the manufacture of printer's ink and especially of motor-car tires. *Lampblack* is similar to carbonblack, but is made by burning oil in a limited supply of air and collecting the smoke in settling chambers.

**Properties of carbon.** The various forms of carbon are all odorless, tasteless solids. They differ, however, in many properties, especially in color, density, and hardness. Carbon is insoluble in all ordinary solvents. Some of the metals, such as iron, gold, and silver, when melted, dissolve it, forming a solution from which the carbon can be separated unchanged. Melted iron is the best solvent, dissolving about 1 per cent of its weight of carbon. In the form of boneblack or charcoal, carbon has the property of absorbing relatively large quantities of certain gases. Similarly, it absorbs certain kinds of organic matter from their solutions. Thus water colored with litmus, when heated with boneblack and filtered, is entirely decolorized.

Carbon is characterized by its great stability toward heat; nevertheless, at high temperatures it has a perceptible vapor pressure. At the temperature of the electric arc (about 3500°) its vapor pressure is greater than the atmospheric pressure, so that at this temperature carbon rapidly vaporizes, passing directly from the solid into the gaseous state.

**Activated charcoal.** All charcoal possesses the power of absorbing gases to a greater or less extent, depending primarily upon the amount of surface exposed in unit volume of charcoal. During the World War great effort was made to prepare for use in gas masks a charcoal in which this property was highly developed. It was found that this could be done by using a very definite heat treatment in the preparation of the charcoal and then *activating* the product by heating it in the presence of a little air; or in some cases steam was used in place of air. Such charcoal is known as *activated charcoal*. It is very porous and absorbs large volumes of gases. The best charcoal for this purpose is made from some very dense material like coconut shells and peach stones.

Near the close of the war the Germans prepared a superior grade of charcoal for use in gas masks by dipping wood, before carbonizing it, into a solution of hydrochloric acid containing a little zinc chloride.

**Chemical conduct.** At ordinary temperatures carbon is a very inert substance, but at higher temperatures it combines directly with most of the elements, such as oxygen, hydrogen, sulfur, silicon, chlorine, and many metals. Because of its strong affinity for oxygen it is an excellent reducing agent. The compounds of carbon with the metals are called *carbides*. One of the most important of these is calcium carbide ( $\text{CaC}_2$ ), used so largely in the preparation of acetylene. When heated in the presence of oxygen, carbon burns, forming carbon dioxide, with evolution of heat as expressed in the following equation



**Uses of carbon.** The chief use of amorphous carbon is for fuel, to furnish heat and power for all the uses of civilization. An enormous quantity of carbon, in the form of coal, coke, and charcoal, is used as a reducing agent in the separation of the various metals from their ores. Carbonblack is used in the

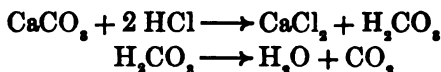
making of motor-car tires, indelible ink, printer's ink, and black varnishes, while boneblack and charcoal are used in filters. In the refining of sugar the dark solution of the impure compound is filtered through layers of boneblack, which removes the coloring matter. On evaporation the resulting solution yields the colorless sugar. Reference has been made to the use of charcoal in gas masks. These masks are now being used to protect workmen in various industries from the evil effects of poisonous gases evolved in industrial operations.

**Carbon dioxide ( $\text{CO}_2$ ).** Carbon dioxide, frequently called *carbonic acid gas*, is the best-known oxide of carbon. A second oxide,  $\text{CO}$ , called *carbon monoxide*, will be discussed in a later chapter.

**Occurrence.** Carbon dioxide is present in the open air to the extent of from 3 to 4 parts in 10,000, and this apparently small percentage is of fundamental importance in nature. For while the *percentage* of carbon dioxide in air is small, the *total amount* in the atmosphere is very large, being estimated at about 2,200,000,000,000 tons. In some localities it escapes from the earth in great quantities, and many spring waters contain it in solution. When such waters reach the surface of the earth, the pressure upon them is diminished, and the gas escapes with effervescence. Carbon dioxide is a product of the oxidation of all organic matter, and is therefore formed in the process of combustion as well as in that of decay. It is exhaled from the lungs of all animals in respiration, and is a product of many fermentation processes, such as that which takes place in the manufacture of alcoholic liquors.

**Preparation.** In the laboratory carbon dioxide is prepared by the action of an acid, such as hydrochloric or sulfuric, upon calcium carbonate ( $\text{CaCO}_3$ ), which occurs abundantly in nature in the form of limestone and marble. The latter, being nearly pure calcium carbonate, is more frequently used. When hydrochloric acid is added to marble, calcium chloride ( $\text{CaCl}_2$ ) and a very unstable compound known as carbonic acid ( $\text{H}_2\text{CO}_3$ ) are

formed. This acid at once decomposes into water and carbon dioxide. The latter, being but moderately soluble, escapes and may be collected by displacement of air or water. The equations for the reactions are as follows:



On a large scale the gas is prepared by a different method. The reactions involved can be studied best in connection with the compounds of sodium which are utilized in its manufacture; accordingly the description of the method will be given in the chapter dealing with these compounds. Prepared on a large scale the gas is compressed in strong iron cylinders, and in this form it is a common article of commerce.

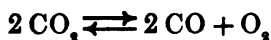
**Apparatus.** To prepare the gas in the laboratory, pieces of marble are placed in the generator *A* (Fig. 17), and commercial hydrochloric acid, diluted with an equal volume of water, is added slowly through the funnel tube *B*. The gas escapes through *C* and may be collected in cylinders. The Kipp apparatus (Fig. 18) is much more convenient.

**Properties.** Carbon dioxide is a colorless, practically odorless gas 1.5 times as heavy as air. One liter of it weighs 1.9768 g. Its high density compared with that of air may be inferred from the fact that it can be siphoned or poured like water from one vessel downward into another. At 15°, and under ordinary pressure, 1 volume of water dissolves about 1 volume of the gas. Its solubility increases regularly *in proportion to the pressure* until about 5 atmospheres is reached; its solubility then becomes abnormally great. The solution has a somewhat biting, pungent taste. At ordinary temperature (20°) carbon dioxide is liquefied by a pressure of 56.3 atmospheres. Its critical temperature is 31.35°, and at this temperature it is liquefied by a pressure of 77 atmospheres. Liquid carbon dioxide is colorless and slightly lighter than water. The liquid dissolves some organic substances, such as naphthalene and camphor, but only a few inorganic substances. The commercial carbon dioxide, compressed in steel

cylinders, is under such great pressure that it is largely in the liquid state. When the pressure is removed, the rapid evaporation of the gas reduces the temperature sufficiently to freeze a portion of the escaping liquid to a snowlike solid. Under ordinary pressures this solid evaporates, without melting, at 78.5°.

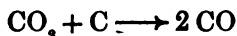
**Solid carbon dioxide.** It is a very simple matter to obtain this solid carbon dioxide and to show its low temperature by freezing mercury with it. Iron cylinders filled with carbon dioxide under pressure are inexpensive and easily available. To obtain the solid carbon dioxide the cylinder should be placed across a desk and supported in such a way that the end provided with a stopcock is several inches lower than the other end. A loose bag is made by holding the corners of a piece of cloth tightly around the neck of the stopcock. Upon opening the stopcock the liquid, together with the gas formed by its rapid evaporation, rushes out. The heat absorbed by the evaporation freezes a portion of the liquid, which is strained out from the gas by the cloth bag. A considerable quantity of the snow very soon collects in the bag. Mercury may be frozen by this snow in the following way: A filter paper is placed in the bottom of a small evaporating dish and some mercury is poured upon it. One end of a piece of wire is wound into a flat coil and dipped into the mercury. A quantity of the solid carbon dioxide is placed upon the mercury and from 10 to 15 cc. of ether poured over it. In this way a temperature of  $-100^{\circ}$  may be obtained, so that the mercury solidifies in a minute or two and may be removed from the dish by the wire which serves as a handle. While the solid carbon dioxide is intensely cold, it may be handled without danger, because the skin is protected from direct contact with it by a layer of gas. The ether is added to the snow in freezing mercury, since in this way better contact is secured.

**Chemical conduct.** Carbon dioxide is a very stable substance. At high temperatures partial decomposition takes place, as expressed in the following equation:

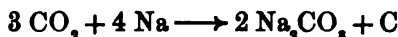


At  $2000^{\circ}$ , under a pressure of 6 atmospheres, about 5 per cent of the carbon dioxide is thus decomposed. It will not combine with oxygen and is therefore incombustible; neither will other substances burn in it under ordinary conditions, for although it contains a large percentage of oxygen, this is held in very firm combination. A few energetic reducing agents remove at least

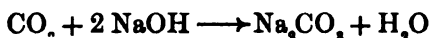
a part of its oxygen. Thus, if it is passed over carbon at temperatures above  $1000^{\circ}$ , the gas is partially reduced, forming carbon monoxide:



At high temperatures sodium reduces carbon dioxide to carbon:

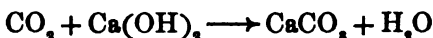


One of the most important reactions of carbon dioxide is that which takes place when the gas is bubbled through aqueous solutions of certain metallic hydroxides. With sodium hydroxide, for example, the reaction is represented by the following equation:



The resulting compound  $\text{Na}_2\text{CO}_3$ , known as sodium carbonate, remains dissolved in the water present. It is evident that if the solution of sodium hydroxide is placed in a suitable tube and the tube and contents weighed both before and after exposure to carbon dioxide, the increase in the weight will be exactly equal to the weight of the carbon dioxide absorbed. This reaction serves as a convenient method for determining the amount of carbon dioxide present in any gas. Since both the sodium hydroxide used and the sodium carbonate formed are white solids, readily soluble in water, no change in the appearance of the solution will be noted during the absorption of the carbon dioxide.

If a solution of calcium hydroxide (ordinary limewater) is used, the reaction takes place just as with sodium hydroxide, and is as follows:



The resulting calcium carbonate,  $\text{CaCO}_3$ , however, differs from sodium carbonate in that it is not soluble in water; hence it separates as fast as formed, and, being a white solid, it causes the solution to become cloudy or "milky" in appearance. If, therefore, we wish to determine whether or not carbon dioxide is present in a gas, it is only necessary to bubble the gas through a clear solution of calcium hydroxide. If carbon dioxide is

present, the solution will soon become cloudy. Barium hydroxide ( $\text{Ba}(\text{OH})_2$ ) acts just as calcium hydroxide, and in some respects is to be preferred in testing for carbon dioxide.

**Quantitative determination of carbon and hydrogen.** Fig. 52 illustrates the method used by a chemist in determining the amount of carbon and hydrogen (say) in a sample of coal. A small amount of the sample is weighed out in a narrow porcelain dish *A* and slipped into the glass tube *B*. The remaining part of the tube is filled with an oxidizing agent, usually copper oxide. The glass tube *B* is gradually heated to a red heat, while a slow current of air, dry and free from carbon dioxide, is passed continuously into the tube at *C*. Under these conditions the carbon and the hydrogen

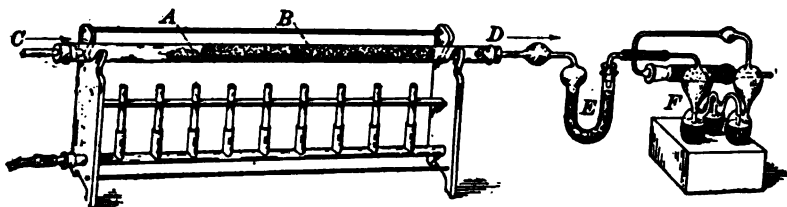


FIG. 52

in the coal burn to carbon dioxide and water respectively; these products of combustion then pass through the narrow tube *D* into the tube *E* filled with pieces of solid calcium chloride which absorbs the water present. The carbon dioxide passes on into *F* which contains a solution of potassium (or sodium) hydroxide and is absorbed. The increase in the weight of tubes *E* and *F* (and contents) will give respectively the weights of the water and carbon dioxide formed, and from these weights the percentage of hydrogen and carbon present can be calculated.

**Uses of carbon dioxide.** Carbon dioxide is used chiefly in the manufacture of soda water and similar beverages, and as a fire extinguisher. Ordinary soda water is simply water charged with carbon dioxide under pressure of from 3 to 4 atmospheres. When the pressure is removed, the excess of gas escapes, producing *effervescence*. Some of the portable fire extinguishers are simply devices for generating carbon dioxide. It is not necessary that all the oxygen should be kept away from a fire in order to smother it. A burning candle, for example, is extinguished in air which contains only 2.5 per cent of carbon dioxide.

**Fire extinguisher.** The general type of the portable fire extinguisher is shown in Fig. 53. The liquid is a solution of sodium hydrogen carbonate

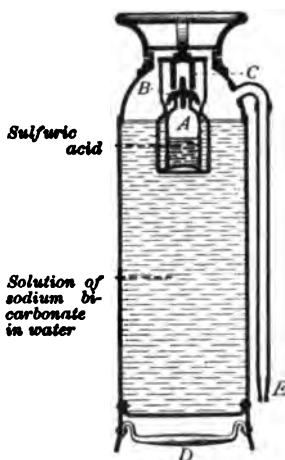


Fig. 53

( $\text{NaHCO}_3$ ) in water. The bottle *A* contains sulfuric acid in sufficient amount to react with the sodium carbonate in solution. In case of fire the vessel is caught by the handle *D* and inverted. The stopper *B* at once drops onto the support *C*, thus allowing the acid to flow out into the larger container. The sulfuric acid immediately reacts with the carbonate, generating carbon dioxide in accordance with the following equation:



Some of the gas dissolves in the water, while the remainder forces the solution out through the nozzle *E*. While the total quantity of water furnished by such an extinguisher is comparatively small, it is

very effective as a fire extinguisher, because of the large percentage of carbon dioxide which it contains in solution.

### QUESTIONS

1. Different varieties of carbon evolve different amounts of heat when burned. How do you explain this fact?
2. Suppose you wished to determine the amount of carbon in a sample of coal or wood. Suggest a possible method of procedure. Would your proposed method tell whether the carbon is present in the sample in the free state or in the combined state?
3. Suggest a reason why the solubility of carbon dioxide is abnormally great under high pressure.
4. In Fig. 52 would it make any difference if the position of the tubes *E* and *F* were interchanged?
5. At ordinary temperatures ( $20^\circ$ ) what is the pressure exerted by the gas in a cylinder of carbon dioxide as sold commercially?

### PROBLEMS

1. (a) What weight of pure carbon would be required to prepare 100 l. of carbon dioxide at  $20^\circ$  and 750 mm.? (b) What weight of pure marble would be required to prepare the same amount of the gas?

2. It is estimated that over 1 billion tons of coal is consumed annually. (a) Upon the supposition that the coal consumed averages 80 per cent carbon, what weight of carbon dioxide would be added to the atmosphere in the combustion of 1 billion tons? (b) How would this amount compare with the total amount estimated to be present in the atmosphere?

3. (a) Upon the supposition that 1 l. of water at 20° and 760 mm. dissolves 1 l. of carbon dioxide, how many liters of the gas would 10 l. of water dissolve under a pressure of 4 atmospheres? (b) What weight of marble would be required for the preparation of this amount of the gas?

4. Calculate the percentage of carbon and hydrogen present in a fuel from the following data: 1.5236 of the fuel was burned as in Fig. 52. The increase in the weight of tube *E* amounted to 0.4012 g. while that of tube *F* was 3.9182 g.

5. A portable fire extinguisher (Fig. 53) contained 5 kg. of sodium hydrogen carbonate. (a) What weight of sulfuric acid would be required to react with this amount of carbonate? (b) What volume of carbon dioxide would be generated, measured at 18° and 752 mm.?

6. When carbon dioxide is reduced to carbon monoxide by means of carbon, how does the volume of carbon monoxide formed compare with the volume of carbon dioxide reduced?

## CHAPTER X

### NITROGEN AND THE RARE ELEMENTS: HELIUM, NEON, ARGON, KRYPTON, XENON

**Historical.** The attention of investigators was first drawn to the general subject of gases by Joseph Black (1728-1799), professor of chemistry in the University of Edinburgh, who discovered the gas now known as carbon dioxide and studied its properties. Following the work of Black we have the investigations of Priestley, Cavendish, Scheele, Lavoisier, and others, which resulted in the discovery of oxygen and hydrogen and in the determination of the composition of water. It was during this period (1772) that Rutherford, professor of botany in the University of Edinburgh, prepared nitrogen and recognized it as a new substance, regarding it, however, as a combination of air with phlogiston. A little later Scheele pointed out that this new substance is a normal constituent of the air. Lavoisier was the first to regard it as an element, and gave to it the name *azote*, a French word signifying that it does not support life. Later the element was found to be an essential constituent of niter (potassium nitrate), and because of this fact Chaptal termed it *nitrogen*, meaning "niter-producing."

**Occurrence.** In the free condition nitrogen occurs in large quantities in the atmosphere, mixed with oxygen and small amounts of other gases. In 100 volumes of dry air there are approximately 78 volumes of nitrogen, 21 of oxygen, and 1 of other gases. In the combined state nitrogen is present in sodium nitrate ( $\text{NaNO}_3$ ) and potassium nitrate ( $\text{KNO}_3$ ), both of which occur in nature in considerable quantities. It is likewise an essential constituent of the compounds known as proteins, which are present in all living organisms. The human body contains 8 per cent of nitrogen.

**Preparation of nitrogen.** Nitrogen may be obtained either from air or from compounds of nitrogen.

1. *Preparation from air.* Nitrogen is ordinarily obtained from air. To separate it from the oxygen with which it is mixed, the air is brought in contact with some substance which combines with the oxygen but has no effect upon the nitrogen. The substances ordinarily used for withdrawing the oxygen are phosphorus and copper, not only because they combine readily with oxygen but also because the oxides formed are solids and thus admit of an easy separation from the remaining nitrogen.

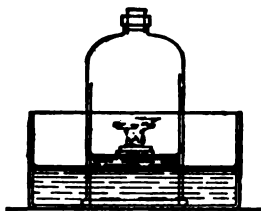


FIG. 54

**Experimental details.** The preparation of nitrogen from air through the action of phosphorus is conveniently conducted as follows: The phosphorus is placed in a small porcelain dish supported on a cork and floated on water (Fig. 54). It is then ignited by contact with a hot wire, and a bell jar is immediately brought over it so as to confine a portion of the air. The phosphorus combines with the oxygen to form an oxide known as phosphorus pentoxide. This is a white solid which floats about in the bell jar; in a short time it is all dissolved by the water, leaving the nitrogen. The withdrawal of the oxygen is indicated by the rising of the water in the bell jar.

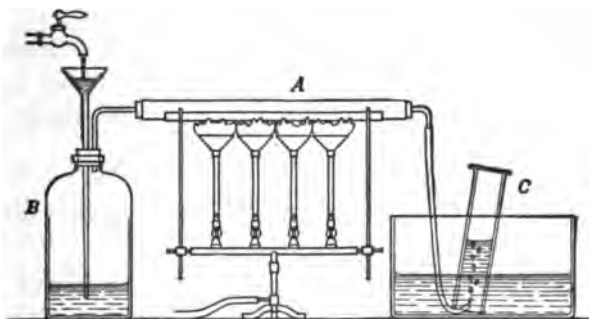


FIG. 55

When copper is used for separating oxygen from the nitrogen, the operation may be conducted as follows: The metal is placed in a tube *A* (Fig. 55) and heated to a high temperature. The air is then forced slowly

through the tube by allowing a small stream of water to flow into a bottle *B* connected with the tube, as shown in the figure. The oxygen combines with the hot copper and forms copper oxide ( $\text{CuO}$ ), a solid which remains in the tube while the nitrogen passes on and is collected over water in a cylinder *C*.

Inasmuch as air contains small percentages of other gases besides oxygen and nitrogen, and since the phosphorus, as well as the copper, removes only the oxygen, it is evident that the nitrogen obtained by these methods is never quite pure; about 1 per cent of the product is composed of other gases, from which it is very difficult to separate the nitrogen. The impure nitrogen so obtained, however, may be used for a study of most of the properties of the element, since these are not materially affected by the presence of the other gases. The most economical way of preparing *pure* nitrogen consists in liberating it from some of its compounds.

2. *Preparation from compounds.* The compound most frequently used for the preparation of nitrogen is ammonium nitrite ( $\text{NH}_4\text{NO}_2$ ). When heated, this compound decomposes into nitrogen and water, as represented in the following equation:



Since ammonium nitrite is not readily kept in the pure state, it is convenient to substitute for it a mixture of sodium nitrite ( $\text{NaNO}_2$ ) and ammonium chloride ( $\text{NH}_4\text{Cl}$ ). These two compounds react to form sodium chloride and ammonium nitrite:



As fast as formed, the ammonium nitrite decomposes into nitrogen and water, as explained above.

**Radicals.** The term *ammonium*, used in the names of such compounds as ammonium chloride, is applied to the group of atoms  $\text{NH}_4$ , which is present in these compounds and acts as a unit. Thus the compound represented by the formula  $\text{NH}_4\text{Cl}$  is called *ammonium* chloride, just as that represented by the formula  $\text{NaCl}$  is called *sodium* chloride. *Such groups of atoms which*

*act together as a unit like an element are called radicals.* These are different from compounds in that they do not exist in a free state. Like the elements, the radicals have definite valences. The ammonium radical  $\text{NH}_4$ , for example, is univalent since it combines with one atom of univalent chlorine ( $\text{NH}_4\text{Cl}$ ). It will be noted that the reaction represented by equation (2) above consists of an interchange between the element sodium and the radical ammonium, both of which are univalent.

**Commercial methods for preparing nitrogen.** It is evident that the method used for preparing oxygen from liquid air (p. 22) will serve equally well for the preparation of nitrogen. This is the method used for preparing the gas on a large scale.

**Properties of nitrogen.** Nitrogen, like hydrogen and oxygen, is a colorless, odorless, tasteless gas. It is slightly lighter than oxygen, 1 l. of it weighing 1.2507 g. Like oxygen and hydrogen it is only slightly soluble in water, 100 cc. of water dissolving 2.38 cc. of the gas under standard conditions. At its critical temperature,  $-146^\circ$ , it is condensed to a liquid by a pressure of 33 atmospheres. Liquid nitrogen is colorless, boils at  $-195.7^\circ$ , and has a density of 0.8 at its boiling point. At a still lower temperature it may be obtained in the form of an icelike solid melting at  $-210^\circ$ .

**Chemical conduct.** Nitrogen is much less active than oxygen, showing little or no tendency to combine with any other elements at ordinary temperatures. Nevertheless, at high temperatures and under suitable conditions it combines with many of the elements. Thus, when subjected to the influence of electric sparks or when heated in the presence of suitable catalyzers, nitrogen combines with hydrogen to form *ammonia* ( $\text{NH}_3$ ), and with oxygen to form *nitric oxide* ( $\text{NO}$ ). Nitrogen likewise combines directly with silicon, boron, titanium, and also with most of the metals, notably lithium, magnesium, and calcium. The compounds formed by the union of nitrogen with another element are in general termed *nitrides*, just as the compounds formed by the union of oxygen with another element are termed *oxides*.

**The assimilation of nitrogen by plants.** While nitrogen is an essential constituent of both plants and animals, yet, with the exception of a few plants, especially those belonging to the natural order *Leguminosæ*, these organisms have not the power of directly assimilating free nitrogen from the atmosphere, but obtain their supply from certain compounds of nitrogen. It has long been known that some of the leguminous plants, such as the beans, peas, and clover, not only thrive in poor soil but at the same time enrich it. Investigation has shown that these plants obtain at least a portion of their supply of nitrogen

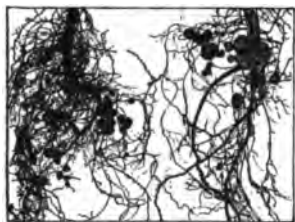


FIG. 56

from the atmosphere. The assimilation of nitrogen is accomplished through the agency of groups of microorganisms which are gathered on little tubercles on the roots of the plants (as represented in Fig. 56, which shows the tubercles on the roots of a variety of bean). These microorganisms have the power of

converting free nitrogen taken from the air into compounds of nitrogen, some of which are assimilated by the plant, while others are left in the soil and thus enrich it.

**Uses of nitrogen.** Free nitrogen is used to a limited extent in the preparation of certain nitrogenous compounds employed as fertilizers (see cyanamide). During the World War the Germans used large quantities of the gas in the manufacture of ammonia, which was used in making nitric acid, and this, in turn, in making explosives. Mercurial thermometers designed for use at temperatures of from  $300^{\circ}$  to  $500^{\circ}$  are filled (over the mercury) with nitrogen under pressure. In this way the mercury is prevented from rapid evaporation, even at temperatures considerably above its ordinary boiling point ( $357^{\circ}$ ). The expansion of nitrogen itself, according to the law of Gay-Lussac, is also utilized as a measure of temperature, at points above the range of a mercurial thermometer. Nitrogen is also used in certain gas-filled electric lamps.

THE RARE ELEMENTS IN THE ATMOSPHERE: HELIUM,  
NEON, ARGON, KRYPTON, XENON

The elements named above are all present in the atmosphere. Because of the minute amounts present, however, and also because of the similarity in properties between these elements and nitrogen, they were not discovered until recent years. They resemble nitrogen in that they are colorless, odorless, tasteless gases and difficult to liquefy. *They are characterized by their complete chemical inertness.* Although subjected to the action of many other substances under conditions which have been most favorable for effecting the combination of elements, no one has yet succeeded in preparing any compounds of these elements. A summation of some of the main facts in reference to these inactive gases is given in the table on page 158.

**Argon.** Argon is found in the air to the extent of 0.937 volumes of the gas in 100 volumes of air. Oxygen prepared from liquid air contains as much as 3 per cent of argon and constitutes the most economical source for the preparation of the gas in quantities. One liter of argon weighs 1.7809 g. It boils at  $-186^{\circ}$  and at still lower temperatures forms an ice-like solid, melting at  $-188^{\circ}$ . The gas is now prepared in considerable quantities and is used in the gas-filled electric lamps which have come into use so largely in recent years.

**Historical.** Attention has been called to the fact that oxygen and nitrogen combine under the influence of electric sparks to form nitric oxide (p. 153). In 1785, in the course of his experiments on air, Cavendish passed electric sparks through an inclosed volume of air (nitrogen and oxygen), introducing more oxygen from time to time, so as to make sure that the quantity of oxygen present would be sufficient to combine with all the nitrogen. After repeated sparking, the oxides of nitrogen formed by the union of the gases, together with the excess of oxygen, were removed by absorbing them in appropriate liquids. In this experiment Cavendish observed that even after repeated trials there still remained a small residue of gas, in volume about  $\frac{1}{15}$  of the air taken, which would not combine with oxygen, and therefore presumably was not nitrogen. No attention was paid to this observation until 1894, when Lord Rayleigh observed that 1 l. of nitrogen

prepared from its compounds weighed 1.2507 g. while 1 l. prepared from the air weighed 1.2572 g. After repeating his experiments a number of times, always with the same results, Rayleigh concluded that the most reasonable explanation of the difference in the weights of the gas obtained from the two different sources lay in the supposition that the nitrogen which he obtained from air contained a small amount of some gas heavier than nitrogen. This conclusion recalled the experiments of Cavendish, and it was thought that perhaps the residue of gas which Cavendish obtained in his experiment was the same which caused the higher density of the atmospheric nitrogen. Acting on this assumption, Rayleigh and the English chemist Ramsay attempted to isolate any unknown gas which might be mixed with the atmospheric nitrogen. Rayleigh employed the method of Cavendish, while Ramsay attempted to separate the unknown gas by repeatedly passing the atmospheric nitrogen over heated magnesium, which combines readily with nitrogen. Without going into detail, it is sufficient to state that both investigators succeeded in showing that the atmospheric nitrogen, as ordinarily prepared, in reality contains a small percentage of gas differing from nitrogen in that it has a greater density and does not unite with any other elements. This gas proved to be a new element, to which the name *argon* was given. In its laboratory preparation it has been found advantageous to substitute either calcium or a mixture of calcium oxide (lime), magnesium, and sodium for the magnesium which Ramsay used for removing the nitrogen.

**Helium.** This element is present in the atmosphere but in much smaller quantities than argon. It is also present in the gases obtained from many minerals as well as in those escaping from certain springs. Its most abundant source is the natural gas found in certain localities, especially in Texas and Kansas, which contains helium in amounts varying from traces to 1.84 per cent. With the exception of hydrogen, it is the lightest of all gases, one liter of it weighing 0.1782 g. Liquid helium has a density of 0.15 and boils at  $-268.7^{\circ}$ . It is the most difficult to liquefy of all known gases. By evaporating liquid helium under reduced pressure a temperature below  $-271^{\circ}$  has been obtained. This is the lowest temperature yet reached and approaches closely to absolute zero.

**Historical.** In 1880 the American chemist Hillebrand found that certain minerals containing the element uranium evolve a gas when heated. He concluded, from a brief investigation, that the gas so evolved is nitrogen.

In 1895, shortly after the discovery of argon, the attention of Ramsay was called to this experiment, with the suggestion that argon might be present in the gas which Hillebrand had obtained. Ramsay repeated the experiment, and upon examination it was found that the spectrum of the gas contained an orange-colored line identical with that which Janssen, in 1868, had detected in the spectrum of the gases surrounding the sun. Lockyer attributed this line to the presence of an unknown element in the sun's atmosphere, which he named *helium*, a word meaning "the sun." Ramsay's experiments proved that the gas evolved from the uranium minerals consists of this same element, helium, mixed with small percentages of argon and nitrogen.

**The preparation of helium.** Until the year 1918, helium had been obtained only in minute quantities. When the United States entered the war an effort was made to find some noncombustible material for the inflation of observation balloons, since the records showed that 95 per cent of the casualties resulting from the operation of such balloons was due to the inflammable character of the filling material. Helium was the only gas that met the requirements, since it is noncombustible and, although about twice as heavy as hydrogen, has a lifting power of 92.6 per cent of that of hydrogen. An effort was made, therefore, to obtain it from the natural gas found in certain localities in Texas. This gas, in addition to the hydrocarbons constituting ordinary natural gas, contains about 35 per cent of nitrogen and approximately 1 per cent of helium. To separate the helium, advantage was taken of its very low boiling point ( $-268.7^{\circ}$ ). By subjecting the natural gas to conditions of pressure and temperature similar to those used in liquefying air, all the constituents of the gas, other than helium, were liquefied, and in this way the separation of the helium was effected. The problem was a very difficult one since the helium gas dissolves in the liquid hydrocarbons and was difficult to separate. When the armistice was signed, however, 147,000 cu. ft. of helium, 93 per cent pure, stored in steel cylinders, was on its way to our armies, and the gas which was almost a chemical curiosity at the beginning of the war was being prepared in quantities.

**Neon, krypton, and xenon.** Following the discovery of argon and helium an exhaustive examination of various gases was made, especially of those obtained from minerals, in the hope that still other elements might be discovered. These investigations proved fruitless until finally directed to liquid air as a possible source of such unknown elements. Large quantities of liquid air were subjected to careful fractional distillation and the different fractions examined, especially by the spectroscope, for the presence of unknown elements. Without going into detail we shall simply note here that by this method Ramsay and Travers, in 1898, succeeded in isolating three new elements, which were named *neon*, *krypton*, and *xenon*,

meaning, respectively, "new," "hidden," and "stranger." These elements proved to be similar to helium and argon in being entirely devoid of chemical activity.

In an effort to discover still other elements in air, Moore examined the heavier gases, first from 19 and later from 100 tons of liquid air, but found no new elements.

Some of the main facts in reference to these inactive gases are given in the following table:

	HELIUM	NEON	ARGON	KRYPTON	XENON
Weight of 1 l. (Watson) . . . .	0.1782	0.9002	1.7809	3.708	5.851
Number of cc. dissolved by 1 l. of water at 20° (Antropoff) . .	13.8	14.7	37.9	78.	110.9
Boiling point of liquid form . .	-268.7°	-239°	-186°	-151.7°	-109°
Melting point of solid form . .	<-271°	-253°	-188°	-169°	-140°
Number of volumes in 1,000,000 volumes of air as estimated by Ramsay . . . . .	4.00	12.3	9400	0.05	0.006

**The spectroscope.** The spectroscope, invented by Bunsen and Kirchhoff in 1860, has been of the greatest service in many chemical investigations, such as those involved in the discovery and isolation of the helium group of gases, so that a brief description of the principle upon which the instrument is constructed and the methods employed in its use will not be out of place here.

When a beam of light passes through a triangular prism of glass, it is bent out of its course and emerges at a decided angle with its original direction, as shown in Fig. 57. Ordinary light is made up of many different

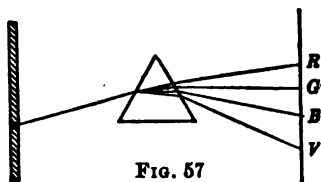


FIG. 57

wave lengths, and each one is deflected, or *refracted*, to a different degree, so that the various colors of which the light is composed are spread out in a series, the red being the least refracted, the violet the most so. A beam of *white* light gives a continuous series of colors from red through orange, yellow, green, blue, to violet, called a *continuous spectrum*. The spectrum of any *colored* light is not continuous, but shows merely those colors of which the light is composed.

That these colors may be made as distinct and sharply separated as possible, the light should shine upon the prism through a very narrow slit in a screen, arranged so as to be parallel with the axis of the prism. The colors will then be a series of narrow lines, each an image of the slit,

spread out parallel with each other. An instrument, the essential parts of which are a prism, a screen provided with a narrow slit, and lenses for focusing the light upon the slit and for viewing the spectrum, is called a spectroscope, or spectrometer. Fig. 58 represents a simple form of such a spectroscope, the slit being seen at the end of the tube *B*. When we look into the eyepiece *A*, the spectrum of the flame is seen as a series of bright lines on a dark field. The tube *C* contains a scale which is also seen when we look into the eyepiece. Any incandescent solid, such as a glowing platinum wire, glowing carbon, or an incandescent lamp, gives a continuous spectrum, all wave lengths of light being represented. Light from volatilized salts and glowing gases gives an interrupted or line spectrum, characteristic of the particular substance giving rise to the light. Each element and many stable compounds may therefore be recognized by their spectrum.

#### Methods of use.

There are a number of ways in which these principles may be applied in practice, depending on the way in which the

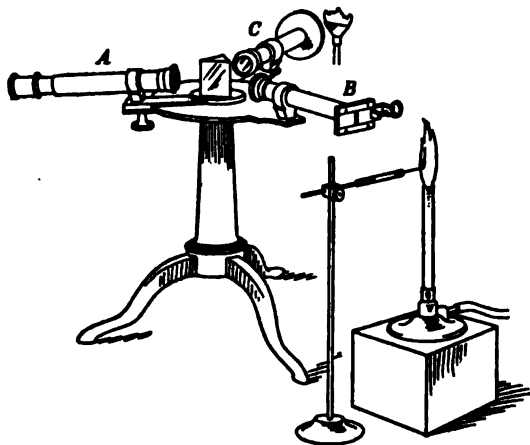


FIG. 58

substance under investigation is brought to the point of giving out light.

1. *Flame spectrum.* The simplest way is to dip a platinum wire into some of the substance, or a concentrated solution of it, and heat the wire in a Bunsen flame. The flame takes on the color of the glowing vapor of the substance, and gives its spectrum when viewed through the spectroscope. When a higher temperature is desired, a little cavity may be hollowed out in the lower carbon of an arc light, and some of the solid placed in this, the heat of the arc slowly volatilizing the solid.

2. *Vacuum-tube spectrum.* When a gas is sealed within a tube provided with electrodes (known as a Plücker tube), such as is represented in *A* (Fig. 59), the pressure of the gas having been reduced to only a few millimeters of mercury before the tube was sealed, a high voltage applied to the electrodes will cause the rarefied gas to become brilliantly luminous. The light in the capillary portion of the tube can be viewed to advantage

in the spectroscope, and a very characteristic spectrum is found for each gas. The character of each spectrum is much influenced by the electrical conditions and by the pressure of the gas, and the variations so produced assist in the identification of any particular gaseous substance. Argon, for example, gives a very complex series of lines. With an intermittent discharge the glow in the tube is red and the red lines in the spectrum are very brilliant; with an oscillating discharge the glow is bright blue,

the red spectrum lines largely disappear, and many new green and blue ones come to view. With helium under a pressure of from 7 to 8 mm. the glow is bright yellow; if the pressure is reduced to from 1 to 2 mm., the tube emits a green light. The current is usually supplied by an induction coil *B* (Fig. 59), operated by a battery.

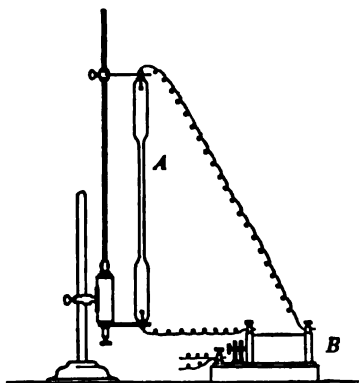


FIG. 59

3. *Absorption spectrum.* It has been stated that an incandescent solid gives a continuous spectrum. If a layer of gas is interposed between the incandescent solid and the prism, the gas will absorb those wave lengths of light which it can itself

give out when luminous, and the continuous spectrum will be interrupted by a series of black lines corresponding to the bright lines of the gas. In this way the solar spectrum is crossed by a great number of dark lines due to the presence of gases in the envelope surrounding the incandescent center of the sun. Such lines are called *Fraunhofer lines*, after their discoverer, and a spectrum in which they appear is called an absorption spectrum. We have learned much about the elements present in the sun from a study of its absorption spectrum.

### QUESTIONS

1. Lavoisier is termed the Founder of Modern Chemistry. Upon what discoveries is this title based?

2. (a) What elements have been studied up to this point? (b) How could you distinguish between them?

3. Would you expect a flash of lightning to cause any chemical reaction to take place in the constituents of the atmosphere? Discuss possible reactions.

4. Liquid air serves as a source for the preparation of what elements?

5. The reactions represented by equations (1) and (2) (p. 152) belong to what type (p. 127)?

### PROBLEMS

1. 10 l. of dry air is passed slowly over hot copper. (a) What is the increase in the weight of the copper? (b) What volume of nitrogen remains?

2. Suppose you wish to prepare 100 l. of nitrogen measured over water in a laboratory at 20° and 750 mm. Calculate the weights of sodium nitrite and ammonium chloride necessary for the preparation of this quantity of the gas.

3. Calculate the difference in weight between the weights of 1 l. of pure nitrogen and 1 l. of nitrogen containing 1 per cent by volume of argon.

4. About 1000 cu. ft. of argon is being used daily in gas-filled lamps. What volume of air is required in its preparation, assuming that all the argon present can be separated?

## CHAPTER XI

### THE ATMOSPHERE

**Atmosphere and air.** The term *atmosphere* is applied to the gaseous envelope surrounding the earth; the term *air* is generally applied to a limited portion of this envelope, although the two terms are often used interchangeably. Many references have been made to the composition and properties of the atmosphere. These statements will now be collected and discussed somewhat more in detail.

**Historical.** Like water, air was first regarded as elementary in character. Near the close of the eighteenth century Scheele, Priestley, Cavendish, and Lavoisier, by their experiments, showed it to be a mixture of at least two gases — those which we now call oxygen and nitrogen. By absorbing the oxygen from an inclosed volume of air and noting the contraction in volume due to the removal of oxygen, Cavendish was able to determine with considerable accuracy the relative volumes of oxygen and nitrogen present.

**The constituents of the air.** The normal constituents of air, together with the approximate amounts of each in samples collected in the open fields, are as follows:

Oxygen . . . . .	21 volumes in 100 volumes of dry air
Nitrogen . . . . .	78 volumes in 100 volumes of dry air
Water vapor . . . . .	variable within wide limits
Carbon dioxide . . . . .	3 to 4 volumes in 10,000 volumes of dry air
Argon . . . . .	0.94 volumes in 100 volumes of dry air
Helium, neon, krypton, xenon	traces

There are also present small quantities of hydrogen, ammonium nitrate, dust particles of various kinds, microorganisms, and probably traces of hydrogen peroxide and ozone. In addition

to these constituents the air in large cities and manufacturing districts contains varying amounts of substances such as hydrogen sulfide ( $\text{H}_2\text{S}$ ), sulfur dioxide ( $\text{SO}_2$ ), and carbon monoxide ( $\text{CO}$ ), which are evolved in the decay of organic matter or are formed in certain manufacturing processes.

For the purposes of discussion it is convenient to divide the constituents of the air into two general classes, the one including those essential to life and the other those not essential.

**The essential constituents.** The constituents which are known to be essential to life are oxygen, nitrogen, water vapor, and carbon dioxide.

The oxygen in the atmosphere directly supports life through the process of respiration. The nitrogen serves to dilute the oxygen and thus to diminish the intensity of its action. It is likewise assimilated by certain plants (p. 154). The water vapor prevents excessive evaporation of the water present in organisms, while the carbon dioxide is an essential plant food.

**The nonessential constituents.** It is unnecessary to comment at length upon these constituents. Some of them, such as the inactive gases described in the preceding chapter, are always present, while others, such as sulfur dioxide and hydrogen sulfide, are found in certain localities only and may be classed as accidental constituents.

Hydrogen peroxide is formed in minute quantities in certain processes of oxidation which are constantly taking place, and any traces of it in the atmosphere are probably derived from this source. The ammonium nitrate is formed by the action of ammonia ( $\text{NH}_3$ ) upon nitric acid ( $\text{HNO}_3$ ). The former of these is a gas evolved in the decay of nitrogenous matter; the latter results from the action of water vapor on an oxide of nitrogen formed by the combination of oxygen and nitrogen during lightning discharges (p. 153). The composition of the dust particles varies greatly, since almost any sort of finely divided material will float in the air. After severe volcanic explosions the atmosphere contains fine volcanic dust for many weeks.

Just as microorganisms occur in all natural waters, so we always find them present in the air. While it is undoubtedly true that transmissible diseases are due to certain kinds of these organisms, it must not be inferred that all microorganisms are a menace to health. The necessary processes of putrefaction and fermentation are due to these organisms and may be prevented when so desired by excluding them. Thus, in the ordinary processes of canning fruits the materials are first heated and then sealed in air-tight receptacles. The heat kills any organisms already present, while the exclusion of air prevents their subsequent introduction from that source. Preservatives are simply substances that prevent the growth of these organisms.

**Methods used for determining the percentages of oxygen, nitrogen, water vapor, and carbon dioxide present in the atmosphere.** The first determinations of the relative amounts of oxygen and nitrogen in air were made by Cavendish in 1783. The method employed consisted in the removal of oxygen from a definite volume of air by means of nitric oxide. This compound possesses the property of combining with oxygen to form a gas known as nitrogen dioxide, which is absorbed by water. The volume of oxygen present in the air was computed from the contraction in the volume of the air due to its removal. This method, however, has given way to other more accurate ones, the most important of which are the following:

1. **Determination of oxygen.** The general method used consists in removing the oxygen from a definite volume of air and noting the contraction in volume. Phosphorus is most often used for removing the oxygen, although copper and hydrogen are sometimes employed. If great accuracy is required, the carbon dioxide present in the sample of air is first removed by sodium hydroxide (p. 146).

**Experimental details.** When phosphorus is used as an absorbent for the oxygen, the determination may be carried out as follows: A tube is filled with water and inverted in a vessel of water (Fig. 60). A sample of the air to be analyzed is then introduced into the tube until it is partly filled.

The volume of the inclosed air is carefully noted and reduced to standard conditions. A piece of phosphorus is attached to a wire and brought within the tube, as shown in the figure. The oxygen combines with the phosphorus, water rising to take the place of the absorbed oxygen. The complete removal of the oxygen is indicated by the fact that no further diminution in the volume of the gas in the tube takes place. The phosphorus is then removed and the volume of the residual gas determined and reduced to standard conditions. The contraction in the volume of the air is equal to the volume of oxygen withdrawn. The time required for the removal of the oxygen is greatly reduced in practice by using a number of strips or wires of phosphorus (p. 33), as well as by using a form of apparatus which makes it possible to cause the inclosed air to flow back and forth over the phosphorus.

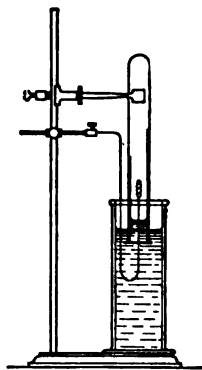


FIG. 60

A more accurate method is the following, in which the oxygen is removed by combination with hydrogen. A eudiometer tube is filled with mercury and inverted in a vessel of the same liquid. A convenient amount of air is then introduced into the tube and its volume accurately noted. There is then introduced more than sufficient hydrogen to combine with the oxygen present in the inclosed air, and the volume is again accurately noted. The mixture is then exploded by an electric spark, and the volume is once more taken. By subtracting this volume from the total volume of the air and hydrogen there is obtained the contraction in volume due to the union of the oxygen and hydrogen. The volume occupied by the water formed by the union of the two gases is so small that it may be disregarded in the calculation. Since oxygen and hydrogen combine in the ratio 1 to 2 by volume, it is evident that one third of the total contraction is equal to the volume originally occupied by the oxygen in the inclosed air. The following example will make this clear:

Volume of air in tube . . . . .	50.0 cc.
Volume after introducing hydrogen . . . . .	80.0 cc.
Volume after combination of oxygen and hydrogen . . . . .	48.5 cc.
Contraction in volume due to combination (80 cc. - 48.5 cc.) . . . . .	31.5 cc.
Volume of oxygen in 50 cc. of air ( $\frac{1}{3}$ of 31.5) . . . . .	10.5 cc.

All these methods agree in showing that 100 volumes of *dry* air contain 21 volumes of oxygen, with a variation of not more than 0.2 per cent.

2. *Determination of nitrogen.* If the gas left after the removal of oxygen from a sample of air is passed over heated magnesium, the nitrogen is withdrawn, argon and the other rare elements being left. It may thus be shown that of the 79 volumes of gas left after the removal of the oxygen from 100 volumes of air, approximately 78 are nitrogen and 1.0 argon. The other elements are present in such small quantities that they may be neglected.

3. *Determination of carbon dioxide.* The method ordinarily used in the determination of carbon dioxide consists in shaking a definite volume of air with a solution of barium hydroxide ( $\text{Ba(OH)}_2$ ). The carbon dioxide reacts with the barium hydroxide to form barium carbonate ( $\text{BaCO}_3$ ), which is insoluble in water, so that it may be filtered off and its weight determined. From this weight it is easily possible to calculate the percentage of the carbon dioxide which was present in the air.

4. *Determination of water vapor.* The water vapor present in a given volume of air may be determined by passing the air over calcium chloride (or some other compound which readily absorbs moisture) and noting the increase in the weight of the absorbing reagent. The percentage present not only varies with the locality, but varies widely from day to day in the same locality, because of the winds and changes in temperature.

**Processes affecting the composition of the air.** The most important of these processes are the following:

1. *Respiration.* In the process of respiration some of the oxygen in the inhaled air is absorbed by the blood and carried to all parts of the body, where it combines with the hydrogen and carbon of the worn-out tissues and of that part of digested food that serves as fuel to supply heat for the body. The products of oxidation are carried back to the lungs and exhaled in the form of moisture and carbon dioxide. The volume of carbon dioxide exhaled by an adult averages about 20 l. per hour.

Hence, in a poorly ventilated room occupied by a number of people the percentage of carbon dioxide increases rapidly. While this gas is not poisonous unless present in considerable amounts, nevertheless air containing more than 15 parts in 10,000 is not fit for respiration.

2. *Combustion.* All the ordinary forms of fuel contain large percentages of carbon. On burning, this carbon combines with the oxygen in the air, forming carbon dioxide.

3. *Decay of organic matter.* The decay of organic matter is largely a process of oxidation brought about through the agency of microorganisms. The carbon and hydrogen are evolved principally in the form of carbon dioxide and water. Any nitrogen present may be evolved as free nitrogen, ammonia, or various oxides of nitrogen, depending upon the conditions. The effect of the decay of organic matter upon the composition of the atmosphere is therefore similar to respiration and combustion in that it tends to diminish the percentage of free oxygen and to increase correspondingly that of carbon dioxide present.

4. *Action of plants.* In the sunlight plants have the power of absorbing carbon dioxide from the air, effecting its combination with water, retaining the carbon and hydrogen, and returning a portion of the oxygen to the air. It will be observed that these changes are just the opposite of those brought about by the processes of respiration, combustion, and decay.

5. *Weathering of rocks.* Large quantities of carbon dioxide are being constantly withdrawn from the atmosphere through its combination with various rock materials.

**The constancy of the composition of air.** Notwithstanding the changes constantly taking place which tend to alter the composition of the air, the results of a great many analyses of air collected in the open fields show that the percentages of oxygen and nitrogen, as well as of carbon dioxide, are very nearly constant. This constancy of composition in the case of oxygen is shown on the following page in the analyses tabulated by Clarke. The percentages are expressed in volumes.

LOCALITY OF SAMPLES	NUMBER OF ANALYSES	MINIMUM OXYGEN	MAXIMUM OXYGEN
Paris . . . . .	100	20.913	20.999
Heidelberg . . . . .	28	20.840	20.970
Manchester . . . . .	32	20.780	21.020
Mountains of Scotland . . . . .	34	20.800	21.180
Dresden . . . . .	46	20.877	20.971
Cape Horn . . . . .	20	20.72	20.970
Cleveland, Ohio . . . . .	45	20.900	20.950

Since the percentages of oxygen and nitrogen in the air are so constant, the question naturally arises whether these two elements are not present in the form of a definite chemical compound. That they are not combined, but are simply mixed together, can be shown in a number of ways, among which are the following:

1. When air dissolves in water it has been found that the ratio of oxygen to nitrogen in the dissolved air is no longer 21 : 78 but more nearly 35 : 65. If air were a chemical compound, the ratio of oxygen to nitrogen would not be changed by solution.

2. A chemical compound in the form of a liquid has a definite boiling point. Water, for example, boils at 100°. Moreover, the steam which is thus formed has the same composition as the water. The boiling point of liquid air, on the other hand, gradually rises as the liquid boils, the nitrogen escaping first, followed by the oxygen.

**Why the air has a constant composition.** If air is a mixture and changes are constantly taking place which tend to modify its composition, how, then, do we account for the constancy of composition which the analyses reveal? This is explained by several facts: (1) the changes which are caused by the processes of combustion, respiration, and decay, on the one hand, and the action of plants, on the other, tend to equalize each other; (2) the winds keep the air in constant motion and so prevent local changes; (3) the total quantity of oxygen and carbon dioxide in the atmosphere is so large as to be practically unaffected by any of the naturally occurring changes.

**Impure air.** Priestley, in his experiments on air, observed that when nitric oxide was introduced into air confined over water, a contraction in the volume of the air took place which he correctly attributed to the absorption of the "dephlogisticated air" (oxygen) by the nitric oxide. This method was therefore used to determine the purity of air (or the goodness, as Priestley termed it), upon the assumption that the percentage of oxygen present in any sample of air is a direct measure of its purity. The kind of tube in which the air was confined in making this determination was termed a *eudiometer* — a word meaning "a measure of goodness," and this term is still retained.

We have long known that Priestley was wrong, since air may be very foul from poor ventilation and yet contain an adequate amount of oxygen. For a long time the injurious effects resulting from inadequate ventilation were attributed to organic matter thrown off from the lungs in the exhaled air. At present, however, it is generally believed that such effects are due almost entirely to high temperatures and to the presence of an abnormal amount of water vapor in the air of the room, both of which conditions are apt to prevail in a poorly ventilated and crowded room.

Not only is water vapor exhaled from the lungs, but there is constant evaporation of moisture from the pores of the skin, and in this process much heat is absorbed. Notwithstanding the extreme changes in the temperature of the air, the temperature of the body in health remains nearly constant. It is partly by variations in the amount of moisture evaporating from the skin that the temperature of the body is maintained at this constant value. If an abnormal amount of water vapor is present in the air, the evaporation of moisture from the skin takes place very slowly, and bodily discomfort follows. Moreover, when the air is perfectly still, that portion of the air in contact with the body tends to become saturated with moisture, and evaporation diminishes; hence the relief that comes from keeping the air in motion, as with an electric fan.

In general, a moisture content of about 70 per cent of that required for saturation is most conducive to comfort. The volume of fresh air necessary for good ventilation varies greatly with conditions, but in general may be said to be about 30 cu. ft. per minute for each person.

The approximate differences in the percentages of oxygen, carbon dioxide, and water vapor in inhaled and exhaled air are shown in the following analyses:

	INHALED AIR	EXHALED AIR
Oxygen . . . . .	21.00%	16.00%
Carbon dioxide . . . . .	0.04%	4.38%
Moisture . . . . .	variable	saturated

**The cycle of carbon in nature.** Under the influence of sunlight the carbon dioxide absorbed from the air by plants reacts with water and small amounts of other substances absorbed from the soil to form complex compounds of carbon which constitute the essential part of the plant tissue. This reaction is attended by the evolution of oxygen, which is restored to the air. The compounds resulting from these changes are much richer in their energy content than are the substances from which they are formed; hence a certain amount of energy must have been absorbed in their formation. The source of this energy is the sun's rays.

If the plant is burned or decays in the open air, the changes which took place in the formation of the compounds present are largely reversed. The carbon and hydrogen combine with oxygen taken from the air to form carbon dioxide and water, while the energy absorbed from the sun's rays is liberated in the form of heat energy. If, on the other hand, the plant is used as food, the compounds present are utilized in building up the tissues of the body and as a source of energy. In either case the carbon and hydrogen ultimately combine with inhaled oxygen to form carbon dioxide and water, which are in turn exhaled. The energy possessed by the food substance is liberated partly in the form of heat, which maintains the temperature of the body, and partly as muscular energy. The carbon originally absorbed from the air by the plant in the form of carbon dioxide is thus restored, and the cycle of changes may be repeated.

### QUESTIONS

1. What contributions to chemistry do you associate with the name of Cavendish?
2. Since much more fuel is burned in the winter than in the summer and since there is but little vegetation to absorb the carbon dioxide in the winter, would you expect the atmosphere to show a larger content of carbon dioxide in the winter time than in the summer?

3. Suppose that a lighted candle was used in place of phosphorus in the experiment illustrated in Fig. 60; would it serve the same purpose as the phosphorus?

4. Give the equation for the removal of  $\text{CO}_2$  from air by  $\text{Ba(OH)}_2$ .

5. Since there is so much water in the world, why is not the atmosphere saturated with water vapor all the time?

### PROBLEMS

1. How would the amount of nitrogen dissolved by water in an atmosphere of pure nitrogen compare with the amount absorbed when exposed to the ordinary atmosphere?

2. Calculate the percentages *by weight* of oxygen and nitrogen present in normal air.

3. The reaction between carbon dioxide and barium hydroxide is represented by the following equation:



A sample of air collected over water measured 10 l. at  $18^\circ$  and 750 mm. This was passed through a solution of barium hydroxide (p. 146); the resulting barium carbonate weighed 0.0211 g. (a) Calculate the weight of the carbon dioxide present in the sample of air. (b) What volume would this occupy when subjected to the conditions under which the sample of air was measured? (c) Compare the volume of the sample of air with that of the carbon dioxide present.

4. A sample of a mixture of oxygen and nitrogen was introduced into a tube graduated in cubic centimeters, inverted in a vessel of water as shown in Fig. 60. The tube was lowered in the water until the level of the liquid inside of it was the same as that outside. The temperature of the gas was  $16^\circ$ , while the barometer in the laboratory read 752 mm. Under these conditions the volume of the gas was 82 cc. A stick of phosphorus was then inserted into the gas as shown in Fig. 60. The water slowly rose in the tube, becoming stationary when the level of the liquid inside the tube was 253 mm. above the level of the liquid in the vessel. The volume of the gas remaining in the tube was then read off and found to be 63 cc. From the above data calculate the percentage by volume of oxygen and nitrogen in the original gas. (The density of mercury is 13.56.)

## CHAPTER XII

### SOLUTIONS

**Introduction.** In Chapter I a distinction was made between a mixture and a compound. In a typical mixture particles of different properties may be distinguished, so it is not of perfectly uniform character. In a compound every smallest portion is identical in composition with every other portion. This must be so, for there is only one variety of molecules present.

Intermediate between these is a great class of bodies called *solutions*, the most familiar types of which are solutions of solids in liquids. They differ most noticeably from mixtures in that they are of perfectly even character throughout, which fact is usually expressed by saying that they are *homogeneous*. They differ from definite chemical compounds in that their composition can be varied between wide limits. A solution may therefore be defined as a *body of homogeneous character whose composition may be varied continuously between certain limits*. It is a body in which molecules of one sort are evenly distributed among those of a different sort.

**Varieties of solutions.** The above definition makes no restrictions as to the physical state of the solution or of its constituents. It includes any combination, such as gases in gases or in liquids, and solids in liquids or in solids. Since there are three general states of matter, there are evidently nine possible combinations, some of which are of small importance. It will be sufficient for our purposes to consider five of the most important pairs.

**Solutions of gases in gases.** We rarely think of a mixture of two gases as a solution, yet it conforms to our definition and in many ways recalls the more familiar case of the solution of

one liquid in another. Regarding it as a solution, we find its properties to be of a very simple character. Save when obvious chemical action occurs, all gases mix in every proportion and apparently have no effect upon each other. If their volumes and pressures are equal before mixing, the mixture will have the double volume if the pressure remains constant. Of this pressure one half will be due to each gas, so that each will exert the same pressure as if it alone had been put in the double volume and the other were not present. When dealing with a solution of gases, therefore, we may assign to each *its fraction of the total pressure*, which will be the same as though the other gases were to be removed, leaving the one alone in the inclosing volume. This fraction of the pressure is called the *partial pressure* of the gas. Thus, as we have seen, the partial pressure of the aqueous vapor in air standing over water at 20° is 17.51 mm. Since there is no expansion or contraction when gases are mixed, the density of the mixture can be calculated from the known densities and percentages of the constituent gases.

**Solutions of gases in liquids.** In this and in the succeeding types of solutions, one of the constituents acts as the dissolving body and is termed the *solvent*; the other acts as the dissolved body, or *solute*. While gases mix with each other in all proportions, a liquid will take up but a limited quantity of a gas. When the gas has been bubbled through the liquid until no more is dissolved, the liquid is said to be *saturated*. Under these conditions the ratio of the quantity of the gas solute to the liquid solvent is called the *solubility* of the gas. This may be expressed in a variety of ways, the most prevalent usage being to state the number of volumes of gas (under definite conditions of temperature and pressure) dissolved in one volume of the solvent. In respect to solubility, gases fall roughly into two classes: those of rather small solubility, such as oxygen, nitrogen, and hydrogen; those of quite large solubility, such as ammonia, hydrogen chloride, and sulfur dioxide. These groups will be discussed separately.

\* SOLUBILITY OF GASES IN 1 LITER OF WATER

NAME OF GAS	VOLUME ABSORBED AT 0° AND UNDER 760 MM. PRESSURE
Ammonia . . . . .	1298.9 l.
Hydrogen chloride . . . . .	506.0 l.
Sulfur dioxide . . . . .	79.79 l.
Hydrogen sulfide . . . . .	4.87 l.
Carbon dioxide . . . . .	1.713 l.
Oxygen . . . . .	0.0489 l.
Nitrogen . . . . .	0.0233 l.
Hydrogen . . . . .	0.0214 l.

**Conditions affecting the solubility of moderately soluble gases.**  
A number of different factors affect the solubility of a moderately soluble gas.

1. *Effect of specific properties.* The specific properties of both gas and solvent are of the first importance in determining the solubility of a given gas in a given solvent. All gases are soluble to some extent in every solvent. Other conditions being equal, no two gases have the same solubility in a given liquid.

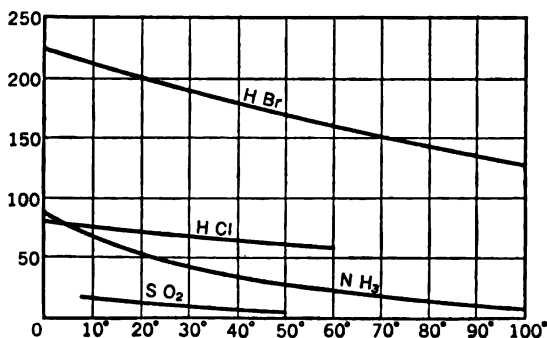


FIG. 61

2. *Effect of pressure; the law of Henry.* Increase of pressure always increases the weight of gas going into solution, the increase

being proportional to the pressure. This is known as the law of Henry, having been formulated by him in 1803. If 1 g. of a gas dissolves in 100 cc. of water at atmospheric pressure, 2 g. will dissolve under 2 atmospheres, provided the temperature remains constant.

8. *Effect of temperature.* With rise in temperature, gases become *less soluble*, and at the boiling point of the solvent most gases are insoluble. This is probably not due to genuine insolubility but to a circumstance explained a little later. The solubility of a gas is not exactly inversely proportional to the temperature, so its value cannot be calculated, but must be determined experimentally at frequent temperature intervals. The results of such experiments are best tabulated in the form of curves (Fig. 61).

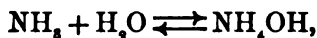
Temperature is represented on the abscissa, and concentrations, in grams per 100 cc., on the ordinate. All the curves show different solubilities at 0°, which diminish as the temperature rises. If solubility were accurately proportional to temperature, it would be represented by a straight line instead of by a curve.

**Conditions affecting the solubility of very soluble gases.** In a qualitative way very soluble gases are affected by temperature and pressure in the same way as are sparingly soluble ones, but quantitatively the law of Henry does not hold, for the solubility is not proportional to the pressure. The specific properties of both gas and solvent play a prominent part, leading to very wide differences in solubility, as may be seen in the table on page 174. There is always a very considerable change in the volume of the solvent when a large volume of gas is absorbed, so it is not possible to calculate the density which such a solution will have, nor from its measured density to infer the weight of gas it has absorbed. Thus, 1 l. of water, when saturated with ammonia at 14°, increases in volume to 1.580 l., while its density decreases to 0.8844.

Solutions of this kind frequently acquire properties possessed by neither the gas nor the liquid. Thus neither ammonia nor water has any effect on the color of red litmus (an organic dye), whereas the solution turns it blue; similarly, sulfur dioxide has no effect on blue litmus, while its solution turns it red. For these and many other reasons it is certain that a chemical action takes place between the gas and the solvent, which accounts for

such high solubility. On the other hand, when the two solutions just mentioned are exposed to the open air, ammonia and sulfur dioxide respectively escape from solution, just as do gases which give no evidence of chemical combination.

**Chemical equilibrium in solution.** The apparently opposite conclusions reached in the last paragraph may be reconciled by assuming that the conditions existing in the liquid resulting from passing ammonia into water are represented by the equilibrium equation



which indicates that the ammonia combines with water to form a compound, ammonium hydroxide ( $\text{NH}_4\text{OH}$ ), but that the reaction is incomplete, owing to the decomposition of the compound into its original components. The equation therefore represents an equilibrium similar to that between oxygen and ozone, or between water and its constituents, oxygen and hydrogen. In a subsequent chapter the conditions which result in such types of equilibrium will be discussed more at length.

**Solubility of mixed gases; the law of Dalton.** When a mixture of several gases is maintained over a liquid, *each dissolves independently of the other and in accordance with its own partial pressure.* This is known as *the law of Dalton*, and its statement was the outcome of some of his earlier experiments, made in 1803. For example, when air is inclosed over water at 760 mm. pressure, approximately  $\frac{1}{5}$  of this pressure, or 152 mm., is due to oxygen, and  $\frac{4}{5}$ , or 608 mm., is due to nitrogen and other gases. According to Dalton's law the quantity of oxygen dissolving in water exposed to air will be the same as if the water were confined in a space containing only oxygen at a pressure of 152 mm. When a solution of a gas other than nitrogen or oxygen is exposed to the open air, the gas will in general escape, for there is no opposing partial pressure to keep it in solution.

It follows that when one gas is bubbled for some time through a solution of a second, the latter will be washed out of the solution, for in the atmosphere over the liquid it exerts no opposing

pressure. When a solution of a gas is boiled, water vapor takes the place of this displacing gas. It bubbles through the solution, maintaining an atmosphere of steam over the liquid, and so prevents a pressure by the dissolved gas. Hence gases are in general insoluble in boiling solvents.

If, however, the gas is a very soluble one, and it happens, in the process of boiling, that the *ratio by weight of the gas to the steam in the atmosphere over the solution comes to be the same as the ratio of the dissolved gas to the water in the solution*, then, since evaporation produces no change in the composition of the solution, the latter will boil without any change in concentration. This happens in a number of familiar instances. For example, a solution of hydrogen chloride boils with constant concentration at  $110^{\circ}$ , when it contains 20.24 per cent of the gas. The gas cannot be boiled out of such a solution.

**Solutions of liquids in liquids.** Two liquids may conduct themselves toward each other in either of two ways: they may be freely soluble (or miscible) in all proportions or each may reach a definite limit of saturation with the other.

**Freely miscible liquids.** A number of familiar liquids mix freely with water in all proportions, among them being alcohol, glycerin, and many acids, such as nitric, sulfuric, and acetic. Many oils and fats are also miscible with each other in all proportions. In some cases, as with alcohol and water, each liquid appears to retain its own chemical characteristics in solution; in other cases, especially with acids dissolved in water, new chemical characteristics are acquired along with the old ones, suggesting the existence of some such chemical equilibrium as that described in connection with ammonia. Several properties of liquid solutions are of importance.

1. **Vapor pressure.** Before mixing, each liquid has its own characteristic vapor pressure at the temperature in question. After mixing, it is found that each liquid has diminished the vapor pressure of the other, so that the vapor pressure of the solution is never as great as the sum of the two original ones.

It may be greater or less than that of either liquid taken separately, or it may have an intermediate value. It also depends on the relative concentrations of the two liquids. In any case the vapor from the solution at any definite temperature will be a mixture of that of each liquid, provided each has a sensible vapor pressure at that temperature.

2. **Boiling point.** On heating a solution of one liquid in another, the total vapor pressure increases, and when it just exceeds the opposing pressure of the atmosphere, the solution boils. From what has been said in regard to the vapor pressure of solutions it will be seen that we can form little idea as to the boiling point of a solution from the known boiling points of its constituents. It may be lower or higher than that of either constituent. Usually it has an intermediate value. Since the ratio by weight of the two vapors escaping from the solution is not in general the same as that of the two liquids constituting the solution, the composition of the liquid will change during the process of boiling. This will lead to variations in the composition of the vapor, and a steady change in boiling point. A solution, therefore, has in general no constant boiling point.

3. **Fractional distillation.** The liquid having the greater vapor pressure will in general pass away from the solution more rapidly than the one of lower vapor pressure (higher boiling point). If the vapors are condensed, as described in the distillation of water, and the resulting liquid is collected in successive portions by changing the receiver at intervals, the first portions will be richer in the more volatile constituent, the higher-boiling liquid being largely obtained in the latter portions. By repeating the process with each portion obtained in the first operation, the two liquids may in time be separated from each other. Such a process is called *fractional distillation*. It is of the greatest importance in many industries, such as the refining of petroleum and the manufacture of alcohol and glycerin. We have already seen that relatively pure oxygen is prepared from liquid air in this way.

**4. Constant-boiling solutions.** It occasionally happens that there is one particular concentration of a solution which has a lower vapor pressure (higher boiling point) than any other concentration, or than that of either constituent taken separately. When such a solution is distilled, one or the other constituent vaporizes more readily and the concentration tends toward that of lowest vapor pressure. When this concentration is reached, the solution boils with constant boiling point like a pure substance, and the distillate has the same composition as the solution remaining in the still. Such a constant-boiling solution cannot be altered in composition by repeated distillation. An example of such conduct is found in aqueous solutions of nitric acid, the constant-boiling solution consisting of 68 per cent acid and 32 per cent water. The constant-boiling solution of sulfuric acid contains 98.33 per cent acid.

**Sparingly miscible liquids.** If water is shaken for a few moments with ether or chloroform in a suitable vessel, such as a separatory funnel (Fig. 34, p. 86), and set aside for a short time, the more or less turbid liquid gradually clears and two liquid layers form, the one of smaller density floating on the heavier. Each of these layers is a saturated solution. In the case of ether and water the upper layer consists of ether saturated with water; the lower, of water saturated with ether. With some pairs of liquids, especially if certain foreign materials are present, this parting into two layers is very slow. The liquid remains turbid and is called an *emulsion*, the name suggesting a conspicuous example, namely, milk. Ultimately the separation takes place, the lighter solution rising to the top.

**Solutions of solids in liquids.** A solid dissolved in a liquid is by far the most familiar type of solution. In the following discussion it should be remembered that we are dealing with true solutions only. Thus it is sometimes said that zinc dissolves in hydrochloric acid. In this case, however, the solution is preceded by an undoubted chemical reaction whereby the zinc is converted into zinc chloride, and it is this compound which is obtained when the solution is evaporated to dryness. With solutions such as we are now considering, evaporation leaves the solute in its original chemical condition.

**Molar solutions.** In stating the concentration of a solution we may obviously make use of the percentage system. It is often more desirable to state the number of formula weights or molecular weights (measured in grams) which a given volume of the solution contains. *When as many grams of a substance as there are units in its molecular weight is dissolved so as to make a liter of solution, it is said to be a molar or gram-molecular solution.* Thus a molar solution of sodium hydroxide ( $\text{NaOH}$ ) contains 40.01 g. of the compound in 1 l., while that of nitric acid ( $\text{HNO}_3$ ) contains 63.02 g. If 15 g. of sodium hydroxide is dissolved so as to form 1 l. of solution, the molar concentration is 0.375 ( $15 \div 40.01$ ).

**Saturated solutions.** When a lump of sugar is placed in a small beaker and covered with water, as represented in Fig. 62, it gradually diminishes in size and passes into solution, particles

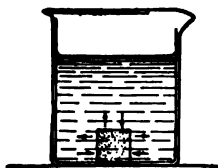


FIG. 62

leaving it and diffusing through the solvent. If there is enough sugar and a long enough time elapses, the concentration of the sugar in the solution reaches a definite limiting value, and we say that the sugar ceases to dissolve and that the solution is *saturated*.

There is good reason for thinking that particles continue to leave the lump, but that an equilibrium has been reached, *the rate of departure of the particles being equal to the rate of their return.* A saturated solution may therefore be defined as *one which is in equilibrium with the undissolved solute.*

It takes a very long time for a solution to become saturated in this way. If a few crystals of a highly colored salt potassium permanganate are placed in the bottom of a tall cylinder, which is then filled with water in such a way as not to disturb them, and the cylinder set aside in a quiet place, months will pass before the color of the solution becomes uniform. If the solvent is stirred or shaken vigorously during solution, saturation may be reached in a short time. The rate at which substances dissolve and reach saturation varies greatly, and it does not bear any very simple relation to the quantity ultimately going into solution. It is dependent on the specific properties of both solute and solvent, on the rate of diffusion of the dissolved substance, on its fineness of division, and doubtless on many other conditions.

That the concentration of a saturated solution at a given temperature has a definite value may be shown by obtaining saturation in still a different way. Most solids are more soluble in hot liquids than in cold. If we approximately saturate a solution at a higher temperature and then reduce the temperature to the desired point, *taking care to have some of the solid present all the time*, the excess of the solute crystallizes out and almost at once the solution comes to the same concentration as was reached in the other slower way.

**Supersaturated solutions.** If we neglect to have any of the solid present during the cooling, it may happen that the excess of solute will fail to crystallize out. The solution will then contain *more than the normal saturation quantity of the solute*, and is said to be *supersaturated*. This is apt to occur in the case of very soluble solids, with salts containing much water of crystallization,—for example, with sodium sulfate ( $\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$ ), sodium thiosulfate ( $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5 \text{H}_2\text{O}$ ), and ferric nitrate ( $\text{Fe}(\text{NO}_3)_3 \cdot 9 \text{H}_2\text{O}$ ),—and, in general, in all cases where the solution becomes notably viscous. It must be remembered that saturation is normally an *equilibrium*. When one member of the equilibrium is absent, abnormal results may be expected. The introduction of even the smallest fragment of the solid solute into a supersaturated solution will bring about the crystallization of the excess of solute. When this is thrown out of solution very rapidly, it appears in a very finely divided form called a *precipitate*, which may be amorphous, but usually consists of minute crystals.

**The solubility of a solid.** Since the concentration of a saturated solution has a perfectly definite value at a given temperature, it may be determined experimentally with great precision. *The ratio between the quantity of solid dissolved and that of the solvent is called the solubility of the solid.* This is usually expressed by stating the weight in grams of the solid that will dissolve in 100 cc. of the solvent at a given temperature. Sometimes it is expressed by stating the weight of the solid in 100 cc. or in 100 g. of the *solution* at saturation.

**Determination of solubility.** The preceding discussion suggests a ready method for determining the solubility of a solid. A saturated solution is prepared, either by long-continued stirring of the solid with the solvent at the desired temperature or by approximately saturating the solvent at a higher temperature and cooling in the presence of the solid. A measured portion of the solution is then filtered off, evaporated to dryness, and the residue weighed.

**Effect of temperature on solubility.** Change of temperature always changes the solubility of a solute. As a rule, solids are more soluble in hot than in cold solvents, though occasionally the reverse is true. Many compounds of calcium, including the hydroxide  $\text{Ca}(\text{OH})_2$ , are of this latter class, while the solubility of common salt is very little affected by the temperature. The table shows the change in solubility in a few familiar cases.

TABLE OF SOLUBILITY OF SOLIDS

SUBSTANCE	FORMULA	WEIGHT DISSOLVED BY 100 CC. OF WATER AT		
		0°	20°	100°
Calcium chloride . . .	$\text{CaCl}_2$	59.5 g.	74.5 g.	159.0 g.
Sodium chloride . . .	$\text{NaCl}$	35.70 g.	36.0 g.	39.80 g.
Potassium nitrate . . .	$\text{KNO}_3$	13.80 g.	31.6 g.	246.0 g.
Copper sulfate . . . .	$\text{CuSO}_4$	14.80 g.	20.7 g.	75.4 g.
Calcium sulfate . . .	$\text{CaSO}_4$	0.759 g.	0.208 g.	0.162 g.
Calcium hydroxide . .	$\text{Ca}(\text{OH})_2$	0.185 g.	0.165 g.	0.077 g.

**Solubility curves.** As a rule, the solubility of a solute does not vary with temperature in any regular manner, so we can best represent the facts in a given case by a curve, plotting the temperature as the abscissa and the concentration as the ordinate. The table (Fig. 63) shows a few typical curves, the concentration being measured by the number of grams of solute dissolved by 100 g. of water. It will be seen that some substances are very soluble, while others are not. The solubility of some increases rapidly with temperature, while in other cases the increase is small.

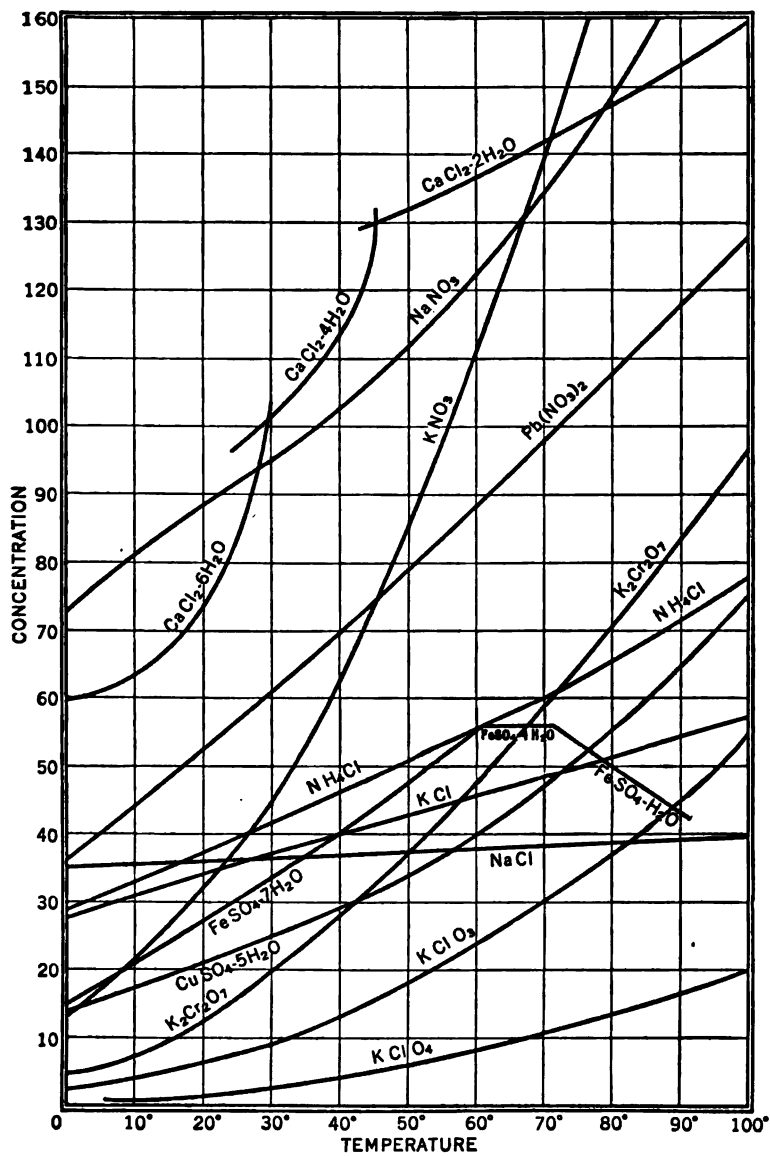


FIG. 68

**Breaks in solubility curves.** The curve for  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  (sodium sulfate) presents a singular feature (Fig. 64). Up to  $32.4^\circ$  it rises rapidly in a normal way, but above that point it steadily falls. An examination of the solids separating above and below this point shows that they are not the same. Below  $32.4^\circ$  the solid is  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ , while above this point it is the anhydrous salt  $\text{Na}_2\text{SO}_4$ . The point  $32.4^\circ$ , therefore, marks the temperature at which the one salt changes into the other; like the freezing point of a liquid, it is called a transition point. Sharp breaks like this in a solubility curve always suggest some chemical transformation in the solute,

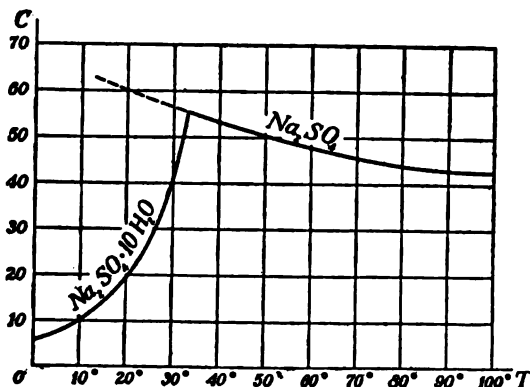


FIG. 64

so that the study of such curves is of much importance in giving information as to the changes taking place in solution.

**Solutions of solids in solids.** A number of cases have been noted in which one solid slowly diffuses into another, much as sugar diffuses into

water. Gold will diffuse into lead when clean pieces of the two metals are tightly clamped together; copperplated zinc gradually turns lighter in color from mutual diffusion of the two metals. The products in such cases are called *solid solutions*. Similar solutions can be prepared in special cases by melting the two solids together. If they form a liquid solution, they may freeze as a homogeneous solid with many of the properties of a true solution. In other cases they do not do this; one solid or the other separates as a pure material, or definite compounds form.

**Solutions of amorphous bodies.** It will be recalled that in Chapter VI amorphous bodies, such as glass, waxes, and glue, were classed as liquids rather than as solids. It is of interest to note that such bodies do not, as a rule, have a definite solubility. They are apt to mix with a solvent in all proportions,

as is true of glue, the solution gradually drying up to a semi-solid form as the solvent is evaporated. This conduct is more like that of one liquid dissolved in another than of a solid dissolved in a liquid. Bodies forming solutions of this kind are called *colloids*, from the Greek word meaning "glue," and their solutions are called colloidal solutions (see Chapter XXXI). Glues, pastes, and jellies belong to this class.

**Regularities observed in solutions.** A careful study of the physical properties of solutions, particularly those of solids in liquids, has brought to light regularities which have led to the development of certain theories regarding the nature of solutions. *These regularities are confined to dilute solutions, and they do not hold good when the solute belongs to either of the three classes of compounds known as acids, bases, and salts, or, collectively, as electrolytes.* A discussion of solutions of electrolytes will be postponed until a later chapter.

1. **Freezing point of solutions.** It has been known for a very long time that the freezing point of a solution is lower than that of the pure solvent. Doubtless one of the first observations of this kind was that salt water remains unfrozen, while fresh water close by freezes. Since the time of Blagden, who was secretary to Cavendish, it has been known that the lowering of the freezing point of a solution is proportional to the concentration. For example, the freezing point of a 2 per cent solution of sugar is twice as much below zero as that of a 1 per cent solution, and that of a 3 per cent solution is three times as much below zero.

If, instead of measuring the concentrations in percentages, we express them in *molar concentrations*, most interesting results are obtained. It is found that the lowering of the freezing point of a definite weight of a solvent, such as water, produced by a *molar weight* of glycerin and of sugar is the same. *If molar weights of solutes (aside from electrolytes) are dissolved in a definite weight of a given solvent, the freezing point of the solvent is lowered equally in all cases, within the limits of unavoidable*

error. This generalization is known as the *law of Raoult* and was formulated in 1883. In the case of water, the freezing point is lowered  $1.87^{\circ}$  by a molar weight per liter of any nonelectrolyte. The following table illustrates this law:

LOWERING OF THE FREEZING POINT OF WATER

SOLUTE	FORMULA	LOWERING PRODUCED IN 1000 CC. OF WATER BY 1 MOLAR WEIGHT OF SUBSTANCE
Methyl alcohol . . . . .	$\text{CH}_3\text{O}$	$1.90^{\circ}$
Ethyl alcohol . . . . .	$\text{C}_2\text{H}_5\text{O}$	$1.87^{\circ}$
Cane sugar . . . . .	$\text{C}_{12}\text{H}_{22}\text{O}_{11}$	$2.02^{\circ}$
Milk sugar . . . . .	$\text{C}_{12}\text{H}_{22}\text{O}_{11}$	$2.06^{\circ}$
Acetone . . . . .	$\text{C}_3\text{H}_6\text{O}$	$1.92^{\circ}$

2. *Lowering of the vapor pressure.* Raoult found that a similar law holds for the lowering of the vapor pressure of a solvent. *If molar weights of solutes (which are neither electrolytes nor liquids with sensible vapor pressures) are dissolved in a definite weight of a given solvent, the vapor pressure of the solvent is lowered equally in all cases.* The lowering is independent of the chemical properties of the substances, but depends merely upon the numerical ratio of the two kinds of molecules which constitute the solution.

**Deliquescence.** When exposed to moist air many solids absorb water to such an extent that they gradually pass into solution. This spontaneous process is called *deliquescence*, and the solid is said to be *deliquescent*. The explanation of this process affords an interesting application of the law of Raoult.

Apparently all solids tend to condense a film of moisture on their surface, and the film soon becomes a saturated solution by dissolving the solid. *If the solid is very soluble*, the solution so formed will be very concentrated, and its vapor pressure very small. If the vapor pressure of the solution becomes smaller than the average value for the partial pressure of the water vapor normally present in air (which may be taken as about

12 mm. at ordinary temperatures), then this solution cannot possibly evaporate. On the contrary, it will absorb moisture from the air. This will dilute the solution, which will then dissolve more of the solid, and the process will continue until all the salt has dissolved.

It will be noticed that the property of deliquescence depends almost entirely upon the molar solubility of the solid and the average humidity of the air, and not upon any specific chemical property. To say that a salt is deliquescent is really to imply that it is very soluble.

3. *Elevation of the boiling point.* Since the boiling point of a liquid is the temperature at which its vapor pressure just exceeds the opposing pressure of the atmosphere, it is evident that any condition which *lowers the vapor pressure will raise the boiling point*, since the liquid will have to be heated higher to return to the original vapor pressure. Lowering of the vapor pressure is found to be almost exactly proportional to rise of boiling point. It follows that molar weights of any substance not an electrolyte and not having a vapor pressure of its own, when dissolved in a definite weight of a solvent, produce the same rise in the boiling point of the solvent. A molar concentration per liter of any nonelectrolyte raises the boiling point of water  $0.54^{\circ}$ .

4. *Osmotic pressure.* We have seen that a substance in solution tends to distribute itself uniformly throughout the entire volume of the solvent. The force which brings about this distribution is called osmotic pressure. We do not, as a rule, notice the existence of any such force or gain any idea as to its magnitude, because it is only when diffusion can be prevented that the force becomes apparent. This can be accomplished by separating a solution from some of the pure solvent by means of a membrane through which the solvent can readily pass, but which restrains the dissolved molecules. Such a membrane is said to be *semipermeable*. Many animal and vegetable membranes are of this sort, so that osmotic pressure plays an important part in physiological processes.

**Qualitative demonstration of osmotic pressure.** A piece of parchment paper is fastened tightly over the bell of a funnel tube by means of windings of cord and sealing wax (Fig. 65). A moderately concentrated solution of sugar is placed in the vessel so constructed, which is then immersed in pure water. The sugar cannot pass through the parchment to distribute itself throughout the water, but the water passes into the bell, the solution rising in the tube until the force of osmotic pressure is balanced by the hydrostatic pressure of the column of liquid.

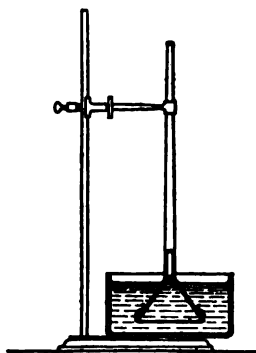


FIG. 65

**Quantitative measurements.** An apparatus such as the one just described is not adapted to the exact measurement of osmotic pressure, because the membrane is not strong enough to withstand the pressure which develops. It has been found that a very satisfactory substitute is obtained by precipitating the compound known as copper ferrocyanide in the pores of a

fine-grained, unglazed porcelain cell similar to a small battery jar. This compound is an amorphous body which is semipermeable, and the walls of the minute pores within which it is precipitated give it the requisite strength. Morse has prepared very perfect cells of this kind by precipitating the copper ferrocyanide by electrolytic methods, the cells withstanding a pressure of as much as 100 atmospheres.

Such a cell is filled with a solution whose osmotic pressure is to be measured; the cell is tightly connected with a pressure gauge, or manometer, and is then immersed in pure water. The water tends to flow into the cell with a force equal to the osmotic pressure, and this is registered on the gauge. Fig. 66 shows the apparatus employed by Morse, *A* being the cell and *B* the manometer.

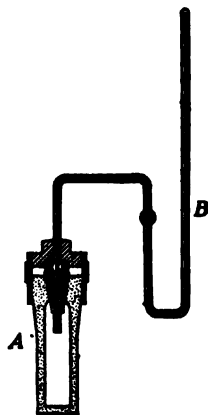


FIG. 66

**The laws of osmotic pressure.** The first quantitative measurements of osmotic pressure were made by the Dutch botanist Pfeffer in 1877, but the more recent work of Morse in America and the Earl of Berkeley in England are of a very much higher order of accuracy. Their results show that within the limits of unavoidable error the

osmotic pressure is proportional to the molecular concentration of the solution, and does not depend upon the character of the solute, provided it is not an electrolyte. It is also proportional to the absolute temperature, so that *the osmotic pressure exerted by a substance in solution is equal to the gas pressure which it would exert if it were a gas occupying the same volume as that of the solvent.* The table gives some of Morse's results, the last column showing how closely the two pressures agree.

OSMOTIC PRESSURE OF CANE SUGAR

MOLAR CONCENTRATION AT 20°	OSMOTIC PRESSURE (Atmospheres)	CALCULATED GAS PRESSURE (Atmospheres)	RATIO OF OSMOTIC PRESSURE TO GAS PRESSURE
0.1	2.590	2.390	1.084
0.2	5.064	4.78	1.062
0.3	7.605	7.17	1.060
0.4	10.137	9.56	1.060
0.5	12.748	11.95	1.067
0.6	15.388	14.339	1.073
0.7	18.127	16.729	1.084
0.8	20.905	19.119	1.093
0.9	23.717	21.509	1.103
1.0	26.638	23.899	1.115

**Summary.** From the foregoing paragraphs it appears that three of the most important of the physical constants of a solvent, namely, the freezing and boiling points and the vapor pressure, are changed to an equal degree by molar quantities of a dissolved substance, and that it is the relative number of the two kinds of molecules, not their character, which determines the extent of the change. Furthermore, the osmotic pressure of a solution is governed by the same numerical ratio and is independent of the character of the substances.

The picture which this presents to us is quite similar to our kinetic idea of gases. The various kinds of molecules appear to distribute themselves throughout the solvent much as a gas distributes itself in the space in which it is inclosed. The osmotic pressure which they produce is quite analogous to the pressure

of a gas, and the other effects are dependent merely upon the number of molecules present in a given volume of the solvent, just as the effects produced by a gas are dependent upon the number of molecules confined in a given space.

### QUESTIONS

1. Explain the formation of small bubbles in water that is being heated, and that form far below the boiling point of the water.
2. Will air pumped out of water contain oxygen and nitrogen in the same ratio in which they occur in ordinary air?
3. How could you tell the difference between a constant-boiling solution and a chemical compound?
4. Is it correct to say that "a saturated solution is one that contains as much of the solute as is possible at that temperature"?
5. Explain the use of alcohol in the radiator of an automobile in cold weather.
6. Wood alcohol has the formula  $\text{CH}_3\text{OH}$  and ordinary grain alcohol the formula  $\text{C}_2\text{H}_5\text{OH}$ . If you had a kilogram of each for use in a radiator, which would be the more effective?
7. If dissolved ammonia is in chemical equilibrium with water, how does it come that *all* the ammonia can be expelled by boiling the solution?
8. Fruit jellies often deposit large quantities of sugar crystals without undergoing any evaporation. How do you account for this?

### PROBLEMS

1. 150 cc. of water was saturated with potassium nitrate ( $\text{KNO}_3$ ) at  $100^\circ$  and was then cooled to  $20^\circ$ . What weight of salt separated?
2. 150 cc. of water, saturated with copper sulfate ( $\text{CuSO}_4$ ) at  $20^\circ$ , was heated in contact with excess of the solid salt to  $100^\circ$ . What weight of salt dissolved?
3. An automobile radiator contained 15 l. of water. If 4 kg. of grain alcohol ( $\text{C}_2\text{H}_5\text{OH}$ ) is added, how much will the freezing point be lowered?
4. Glycerin has the formula  $\text{C}_3\text{H}_8\text{O}_3$  and dissolves in water in all proportions. If I wish to raise the boiling point of a water-bath containing 5 l. of water to the extent of  $10^\circ$ , how much glycerin must I add?

## CHAPTER XIII

### CHLORINE; HYDROCHLORIC ACID; ACIDS; SALTS

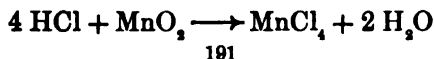
**History and occurrence of chlorine.** The element *chlorine* is a greenish-yellow gas and was first isolated by Scheele in 1774. Because of its activity, it does not occur free in nature; hence when desired it must be liberated from one of its compounds. Scheele obtained it by liberating it from hydrochloric acid (a compound of hydrogen and chlorine) by the action of manganese dioxide, a method of preparation which is still used. The element was regarded, however, as a compound of hydrochloric acid with oxygen until the English chemist Davy, in 1810, proved its elementary character.

Because of its color Davy named the element *chlorine*, from the Greek word meaning "greenish yellow."

The most abundant compound of chlorine is sodium chloride, ordinarily known as common salt. This compound is found in sea waters and in large deposits in various parts of the earth. Chlorine also occurs in nature in combination with potassium, magnesium, calcium, and, to a limited extent, with some of the other metals. Sodium chloride is an essential constituent of our food, while the acid character of the gastric juice is due largely to hydrochloric acid.

**Laboratory methods for preparing chlorine.** Two general methods are used in the laboratory in the preparation of chlorine.

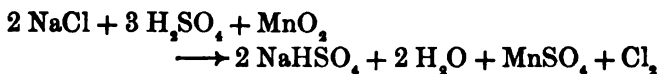
1. *By the action of hydrochloric acid upon manganese dioxide.* When hydrochloric acid is gently heated with manganese dioxide, the hydrogen of the acid and the manganese of the dioxide exchange places as indicated in the following equation:



The resulting compound,  $\text{MnCl}_4$ , known as manganese tetrachloride, is unstable and as fast as formed decomposes into manganese chloride,  $\text{MnCl}_2$ , and free chlorine as follows:



Since sodium chloride and sulfuric acid act upon each other to form hydrochloric acid, it is often found more convenient to substitute a mixture of these two compounds for the hydrochloric acid in the above process. The reaction is then expressed in the following equation:



**Experimental details.** Manganese dioxide and hydrochloric acid are placed in the flask *A* (Fig. 67) and thoroughly mixed. A gentle heat is then applied to the flask. Chlorine is evolved and, escaping through the tube *B*, bubbles through the water in bottle *C* (which removes any hydrochloric acid carried over with it) and finally through some sulfuric acid in bottle *D* (which removes any moisture present).

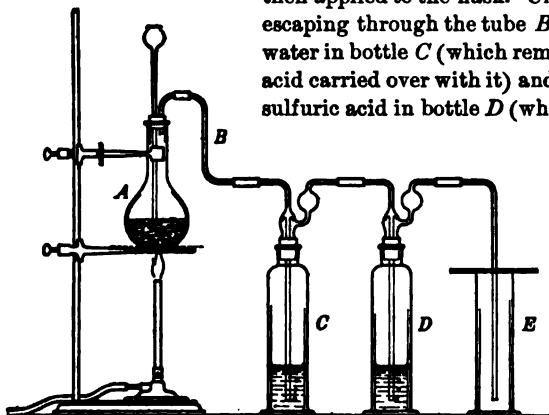
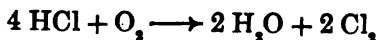


FIG. 67

Since the gas is fairly soluble in water, it is collected by displacing the air in bottles or cylinders *E*. Because of the poisonous character of chlorine, the preparation must be carried on in a well-ventilated hood.

**2. By the action of oxidizing agents upon hydrochloric acid.** Under suitable conditions oxygen acts upon hydrochloric acid, liberating chlorine in accordance with the following equation:

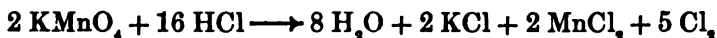


The speed of the reaction between free oxygen and hydrochloric acid is very slow, although it can be greatly increased by a

catalyzer, especially copper sulfate. In the laboratory, however, it has been found more convenient to use some oxidizing agent, such as potassium permanganate ( $\text{KMnO}_4$ ) in place of free oxygen. When this compound is brought together with hydrochloric acid, the oxygen present in the permanganate reacts with the hydrochloric acid in accordance with the above equation, forming water and chlorine. A part of the chlorine combines with the potassium and manganese to form the chlorides  $\text{KCl}$  and  $\text{MnCl}_2$ , while the remainder is liberated in the free state and may be collected in cylinders or bottles. The complete equation for the reaction is as follows:



If the molecular formula for chlorine is desired, the equation then becomes



**Experimental details.** To obtain chlorine in the laboratory by this method the potassium permanganate is placed in a flask *A* (Fig. 68), and a mixture of equal volumes of concentrated hydrochloric acid and water is added, drop by drop, from a separatory funnel *B*. The reaction takes place at once, and the evolved chlorine may be collected by displacement of air. If a high degree of purity is desired, the gas should be passed through sulfuric acid.

**Commercial methods for the preparation of chlorine.** If the eudiometer (Fig. 5) used in the decomposition of water by the electric current, or some similar apparatus, is filled with a solution of sodium chloride and a current of electricity is passed through the solution, the sodium chloride is decomposed into chlorine, which is evolved at the positive electrode (called the *anode*), and sodium, which is set free at the negative electrode (called the *cathode*). The sodium, however, reacts with the

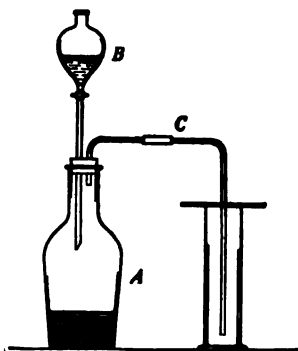


FIG. 68

water present (p. 44) as fast as liberated, forming hydrogen, which is evolved at the cathode, and sodium hydroxide, which remains dissolved in the water. The products of the reaction, therefore, are chlorine, hydrogen, and sodium hydroxide.

This reaction is the one employed in the preparation of all the chlorine used commercially in the United States. The actual apparatus used is called a cell and is of course much larger than the eudiometer and built of more substantial material. Carbon electrodes are also substituted for the platinum ones employed in the decomposition of water.

The chief difficulty in preparing chlorine by this method consists in keeping the chlorine and sodium hydroxide apart; for, on coming in contact, they react upon each other and the

chlorine enters into combination. This difficulty is usually overcome by separating the anode and cathode compartments of the electrolytic cell by a porous diaphragm. A number of different cells have been devised for carrying out the process. These cells are designated by the name of the inventor, so that we have, for example, the Nelson cell, the Allen-Moore cell, the Townsend cell. The latter is described below and will serve to illustrate the general principle involved in the construction and operation of all the cells.

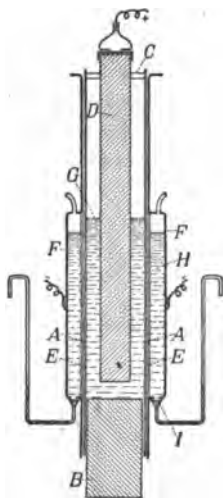


FIG. 69

#### Commercial preparation by the Townsend cell.

A section of this cell is shown in Fig. 69. The anode compartment is formed by the diaphragm *A*, *A*, a nonconducting bottom *B*, and a lid *C*. The diaphragm is made of asbestos cloth painted over with a mixture of iron oxide and asbestos fiber. Through the lid *C* extends the graphite anode *D*. The diaphragm is set firmly against the perforated iron cathode plate *E*, *E*, which is in turn held in place by the iron sides *F*, *F*, the space between the plate and the iron sides forming the cathode compartment. The anode compartment is partially filled with saturated salt solution *G*, and the

cathode compartment with kerosene *H*. Since the level of the salt solution is above that of the kerosene, the solution slowly penetrates the diaphragm, and some of the salt, coming in contact with the cathode, is changed into the hydroxide. The resulting solution of the chloride and hydroxide, being heavier than the kerosene, sinks to the bottom and is drawn off through the side tubes *I*. The chloride, being much less soluble than the hydroxide, is separated by partial evaporation of the solution, and the sodium hydroxide is then recovered. The hydrogen and the chlorine that are set free are led off through tubes.

The hydrogen is sometimes used in preparing hydrochloric acid, but much of it is wasted. The chlorine is either used directly for bleaching or in the preparation of *bleaching powder*, or is pumped into strong iron cylinders and sold commercially in this form. The chlorine plants in the United States have a capacity of about 400 tons daily, much of which is used directly in bleaching wood pulp from which paper is made.

The electrolytic method for preparing chlorine possesses the following advantages: (1) sodium chloride is cheap; (2) in addition to chlorine, sodium hydroxide, for which there is great demand, is formed in the process. The chief item of cost is the generation of the electrical energy, so that the factories for the production of chlorine are likely to be located at points where water power can be used to advantage, as at Niagara Falls.

**Properties.** Chlorine is a greenish-yellow gas and possesses a peculiar suffocating odor. It is 2.49 times as heavy as air, and under ordinary conditions 1 volume of water dissolves about 2.5 volumes of the gas. At ordinary temperatures ( $18^{\circ}$ ) it is liquefied by a pressure of 16.5 atmospheres. Since the commercial chlorine stored in iron cylinders is subjected to a greater pressure than this, it is evident that in these cylinders it is in a liquid state. Liquid chlorine is yellowish in color, boils at  $-38.6^{\circ}$ , under atmospheric pressure, and solidifies at  $-101.5^{\circ}$ . When inhaled in small quantities, chlorine produces the symptoms of a hard cold, and in larger quantities has serious and even fatal effects.

**Chemical conduct.** At ordinary temperatures chlorine is one of the most active of all the elements. The compounds formed by its union with any other element are called *chlorides*.

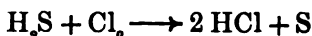
1. **Action upon metals.** Nearly all the metals combine directly with chlorine, especially when heated. A strip of copper

foil, heated to redness and immediately dropped into chlorine, burns with incandescence. Sodium burns brilliantly when heated strongly with moist chlorine. Gold and silver are quickly tarnished by the gas, and even platinum is readily attacked by it.

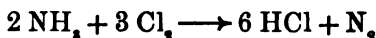
2. *Action upon nonmetals.* Chlorine has likewise a strong affinity for most of the nonmetals. Thus phosphorus and sulfur burn in a current of the gas, while antimony and arsenic, in the form of a fine powder, at once burst into flame when brought in contact with it, forming in each case the chloride of the element.

3. *Action upon hydrogen.* Chlorine unites readily with hydrogen, forming hydrogen chloride. A jet of hydrogen burning in the air continues to burn when introduced into a jar of chlorine, giving a somewhat luminous flame. A mixture of the two gases explodes violently either when heated or when exposed to bright sunlight.

4. *Action upon compounds of hydrogen.* Not only will chlorine combine directly with free hydrogen, but it will remove the element from some of its compounds. Thus, when chlorine is passed into an aqueous solution of hydrogen sulfide, sulfur is precipitated and hydrochloric acid formed, as expressed in the following equation:

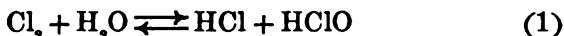


With ammonia the action is similar:

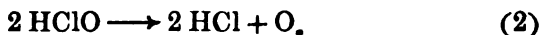


Under certain conditions the nitrogen evolved combines with chlorine to form a very explosive, oily liquid known as nitrogen trichloride. The strong affinity of chlorine for hydrogen is very strikingly shown by its action upon turpentine. This latter substance is made up of compounds containing carbon and hydrogen. When a strip of paper moistened with warm turpentine is placed in a jar of chlorine, the hydrogen and chlorine unite, with evolution of light, forming hydrochloric acid, while a black deposit of carbon remains.

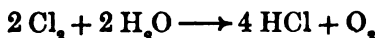
5. *Action upon water.* The liquid resulting from passing chlorine into water is often regarded simply as a solution of chlorine in water and is called *chlorine water*. The chlorine, however, reacts slowly with the water to form a mixture of hydrochloric acid (HCl) and hypochlorous acid (HClO), until the equilibrium expressed in the following equation results:



Hypochlorous acid is unstable, however, and decomposes, slowly in the dark but rapidly in the sunlight, into hydrochloric acid and oxygen:



This removal of the hypochlorous acid through decomposition disturbs the equilibrium expressed in equation (1) so that the interaction of the chlorine and water continues as long as any free chlorine is left. There finally results a dilute solution of hydrochloric acid, as is shown by combining equations (1) and (2). The resulting equation is



The effect of sunlight in increasing the action of chlorine upon water may be shown in the following way: If a long tube of rather large diameter is filled with a saturated solution of chlorine in water and inverted in a vessel of the same solution (as shown in Fig. 70), and the apparatus is placed in bright sunlight, bubbles of gas will soon be seen to rise through the solution and collect in the tube. An examination of this gas will show that it is oxygen.

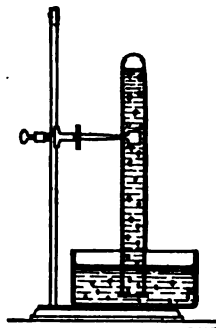


FIG. 70

The decomposition of water through the action of chlorine is also greatly increased in the presence of some substance which combines with the oxygen as fast as it is set free. Consequently, a solution of chlorine in water is a good oxidizing agent, and, indeed, it is often used as such.

6. *Formation of hydrates.* When chlorine is passed into water and the solution is cooled to a point just above freezing, a

crystalline hydrate separates, which has the composition  $\text{Cl}_2 \cdot 8 \text{H}_2\text{O}$ . As the temperature rises, the hydrate gradually dissociates into its constituents. It is interesting to note that it was from this hydrate that Faraday, in 1823, first obtained chlorine in a liquid state, using the form of apparatus shown in Fig. 37 (p. 96).

7. *Action upon color substances; bleaching action.* Chlorine possesses a powerful bleaching action. Strips of highly colored cloth, when moistened with water and placed in jars of chlorine, rapidly lose their color. The presence of water is essential to the change, as may be shown by placing strips of the dry cloth in chlorine, from which the moisture has been removed by bubbling it through sulfuric acid (Fig. 67). Under these conditions the color of the cloth remains unchanged. It is probable that the bleaching action of chlorine is in reality due to the oxidizing action of hypochlorous acid as explained in (5), the resulting oxygen reacting with the color substance of the cloth to form colorless compounds. It is evident, therefore, that chlorine will bleach only those materials whose colored constituents it changes into colorless compounds. It has no bleaching action on such color substances as carbon, and hence does not affect printers' ink made from carbon. It cannot be used for bleaching certain substances like silk, since it injures the fabric.

8. *Action as a germicide.* Chlorine has marked germicidal properties, so that both the free element and the compounds from which it is easily liberated are used as disinfectants.

*Uses of chlorine.* The greatest use of chlorine is as a bleaching agent, large amounts being used especially for bleaching wood pulp, from which much of our paper is made. The various kinds of fabrics woven from vegetable fibers, such as flax and cotton, are always more or less colored by the presence of natural coloring matter. Hence, if a white fabric is desired, bleaching is necessary. This was formerly accomplished by exposing the fabric to the action of air and sunlight, but many days were required for the completion of the process. The same

results are now obtained in a very short time by the use of chlorine. Increasing amounts of the gas are also being used for purifying water on a large scale, as in our city water supplies. In the form of *bleaching powder*, or *chloride of lime*, a compound which readily evolves chlorine, it is used in our homes as a general disinfectant. Considerable amounts of the gas are used in the manufacture of certain compounds such as carbon tetrachloride ( $\text{CCl}_4$ ) and chloroform ( $\text{CHCl}_3$ ).

**Chlorine in the World War.** Practically all the poison gases used in the war were either free chlorine or compounds of chlorine. Poison gas was first used by the Germans, April 22, 1915, when a large quantity of chlorine, previously stored in cylinders and hidden in the trenches, was allowed to escape. The gas, being heavy, clung to the ground and was carried forward by a favorable wind. Later in the war the use of chlorine gave way largely to certain of its compounds, which are more poisonous than the free element. Moreover, in place of trusting to the wind to carry the gas, the compounds were filled into shell and then fired into the ranks of the enemy. Because of the large demand for poison gas, great quantities of chlorine were required. To help meet the demand the United States built at Edgewood, Maryland, in 1917-1918, a chlorine plant with a daily capacity of 100 tons — the largest chlorine plant ever constructed.

**Nascent state.** In discussing the preparation of chlorine it was stated that while free oxygen will decompose hydrochloric acid, forming water and chlorine, the speed of the reaction is very slow, so that this method is not a practical one for the preparation of the gas. If, on the other hand, an oxidizing agent is used and the oxygen is liberated directly in contact with the hydrochloric acid, the reaction proceeds rapidly. This is but one example of many reactions which indicate that the activity of an element is greatest just at the instant of its liberation from its compounds. Elements in this condition are said to be in the *nascent state*, the word *nascent* being derived from a Latin word meaning "to be born." This greater activity is usually explained upon the assumption that an element at the instant of liberation from its compound is in the form of free atoms, and is therefore more reactive than after the atoms have combined to form molecules.

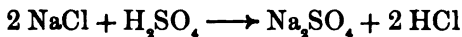
## HYDROCHLORIC ACID; HYDROGEN CHLORIDE

**Distinction between the terms *hydrochloric acid* and *hydrogen chloride*.** The liquid known as hydrochloric acid consists of an aqueous solution of a gaseous compound, which has the formula HCl. In order to distinguish between the gaseous compound and its aqueous solution, the gas is called *hydrogen chloride*, while the term *hydrochloric acid* is reserved for the solution. This distinction is desirable at times, although it is not always made in chemical literature, the term *hydrochloric acid* being used sometimes to designate either the gas or its solution. For example, problems like the following are frequently stated: What weight of hydrochloric acid is required in the preparation of 10 l. of hydrogen? It is evident that in such a problem what is desired is the weight of the hydrogen chloride, since the hydrogen evolved all comes from the hydrogen chloride and not from the water present. In the subsequent pages the distinction will be observed wherever clarity will be gained by so doing.

**Preparation of hydrochloric acid.** Since this acid is prepared by simply dissolving the gas, hydrogen chloride, in water, the question resolves itself into the methods for preparing this gas. Three general methods are used as follows:

1. ***By direct combination of its constituent elements.*** Hydrogen chloride is formed by the direct union of hydrogen and chlorine. Since both these elements are obtained in quantities in the electrolysis of solutions of sodium chloride, this method is used to a limited extent in the preparation of hydrogen chloride on a commercial scale.

2. ***By the action of concentrated sulfuric acid upon chlorides of metals.*** Sodium chloride, because of its low cost, is always used. The reaction is expressed by the following equation:



It will be noted from the equation that sodium sulfate is likewise formed in this process. Now the demand for sodium sulfate is

very great, large quantities of it being used in the preparation of sodium carbonate, as well as in the manufacture of glass. It follows that in the preparation of the sulfate large quantities of hydrogen chloride are produced, and, indeed, this is its most important source. The method also serves as a convenient one for the preparation of hydrogen chloride in the laboratory.

**Laboratory preparation.** Sodium chloride is placed in the flask *A* (Fig. 71), fitted with a funnel tube and an exit tube, sulfuric acid of the proper concentration is added, and the flask is gently warmed. Hydrogen chloride is evolved and is collected by displacement of air, as in the preparation of chlorine. To prepare a solution of the gas, the end of the exit tube is fixed just above the level of some water contained in a cylinder *B*. The gas, being extremely soluble in water, is absorbed as fast as it escapes from the tube. Care must be taken not to have the end of the exit tube dip below the surface of the water, since the solubility of the gas is so great that the water would rush back into the generating flask.

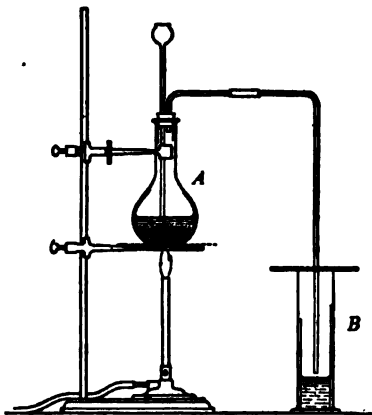
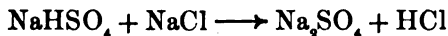


FIG. 71

If the sulfuric acid is added, not to the solid sodium chloride but to an aqueous solution of the salt, there is no very marked action. The hydrogen chloride formed is very soluble in water and so does not escape from the solution unless heated; hence a state of equilibrium is soon reached among the four substances represented in the equation.

**3. By the action of sodium chloride upon sodium hydrogen sulfate.**

This latter compound is obtained in the manufacture of nitric acid. When heated with sodium chloride, hydrogen chloride is obtained in accordance with the following equation:



This method is likewise used for the preparation of hydrogen chloride on a commercial scale.

In the commercial preparation of hydrogen chloride the gas is absorbed in water, in which it is extremely soluble. The resulting solution constitutes the ordinary hydrochloric acid of commerce. When the materials are pure, the solution obtained is colorless. The commercial acid, often called *muriatic acid*, is usually colored yellow by impurities.

**Liberation of hydrogen chloride from its solution.** The pure hydrogen chloride can easily be regained from its aqueous solutions by the addition of sulfuric acid, which diminishes the solubility of the hydrogen chloride.

This serves as a very convenient method for obtaining pure hydrogen chloride when a limited supply of it is desired in the laboratory. The concentrated solution is placed in *A* (Fig. 72), and the flask is connected with the bottle *B*, which contains sulfuric acid for drying the gas. This bottle is fitted with stopper and tubes, as shown in the diagram. The glass tube leading from the bottle *B* to the bottom of the cylinder *E* passes through a perforated cardboard or glass plate *C*, which rests lightly on the top

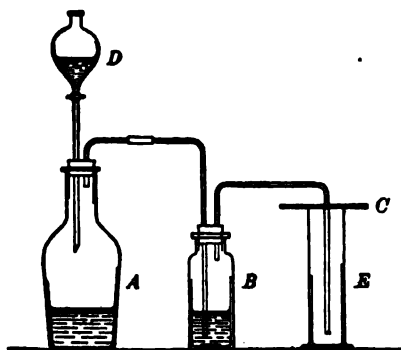


FIG. 72

of the cylinder. Sulfuric acid is now added, drop by drop, from the separatory funnel *D*. The hydrogen chloride is at once evolved and, after bubbling through the sulfuric acid in *B*, whereby any moisture is removed, is collected in *E*, as shown in the figure.

**By-products.** It usually happens that in the preparation of any given substance other compounds are formed. These are called *by-products*. Thus hydrochloric acid is a by-product in the manufacture of sodium sulfate. It is evident that the cost of the manufacture of any substance can be decreased to the extent to which the by-products can be utilized. Indeed, the demand for the by-product may become so great that it really comes to be the main product. The success of a process often depends upon the value of the by-product formed.

**Properties of hydrogen chloride.** Hydrogen chloride, a colorless gas, is 1.26 times as heavy as air. When inhaled it has an irritating and suffocating effect. At  $0^{\circ}$  it is condensed to the liquid state by a pressure of 28 atmospheres. This liquid is colorless, boils at  $-83.1^{\circ}$ , and solidifies at  $-113^{\circ}$ . It does not conduct electricity, has no action upon metals, and in general is very inactive. Hydrogen chloride is very soluble in water, 1 volume of the latter under standard conditions dissolving 506 volumes of the gas. The density of its aqueous solutions increases with the amount of gas dissolved, as shown in the following table, which gives the percentage by weight of hydrogen chloride present in solutions of various densities, the measurements being taken at  $15^{\circ}$ .

PER CENT OF HCl	DENSITY	PER CENT OF HCl	DENSITY	PER CENT OF HCl	DENSITY
5.69	1.0284	20.04	1.1006	35.02	1.1779
10.17	1.0507	25.06	1.1265	40.09	1.2013
15.22	1.0761	30.00	1.1526	43.40	1.2134

A solution of hydrogen chloride in water, containing 20.24 per cent of the gas, has a fixed boiling point, namely,  $110^{\circ}$  (p. 177). Solutions more concentrated than this lose hydrogen chloride, while more dilute solutions lose water until the above concentration is reached, when they boil with unchanged concentration.

**Solubility of hydrogen chloride.** The extreme solubility of hydrogen chloride in water may be shown as follows: A perfectly dry flask *A* (Fig. 73) is filled with hydrogen chloride. This flask is connected, by means of a glass tube, with a similar flask *B*, which is nearly filled with water, as shown in the figure. The end of the tube opening into flask *A* is drawn out to a rather fine jet.

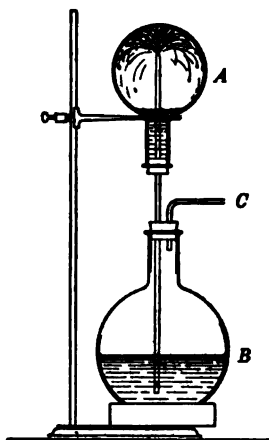
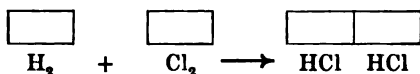


FIG. 73

By blowing into the tube *C*, a few drops of water are forced into *A*. Some of the hydrogen chloride at once dissolves, thus diminishing the pressure inside the flask. The water then flows continuously from *B* into *A*, until practically all the hydrogen chloride is absorbed. It is evident that the connection must be air-tight.

**Composition.** The composition of hydrogen chloride can be determined by the electrolysis of its aqueous solution. When electrolyzed, the hydrogen of the compound is evolved at the cathode and the chlorine at the anode. A special form of apparatus is required, in order to avoid the difficulties arising from the marked solubility of the chlorine in water. When the experiment is carried out, it is found that the volume of the hydrogen liberated is exactly equal to that of the chlorine. Conversely, it is possible to show by experiment that when hydrogen and chlorine combine, they always do so in the ratio of 1 volume of hydrogen to 1 volume of chlorine; moreover, the product is always 2 volumes of hydrogen chloride. These relations may be shown graphically in the following way:



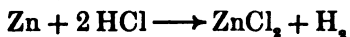
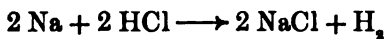
Since chlorine is 35.18 times as heavy as hydrogen, it follows that 1 part by weight of hydrogen combines with 35.18 parts by weight of chlorine to form 36.18 parts by weight of hydrogen chloride.

**Properties of hydrochloric acid.** While hydrogen chloride itself has but little chemical activity, its aqueous solution, namely hydrochloric acid, has marked properties, the most important of which are as follows:

1. **Taste.** A dilute aqueous solution of the acid has a sour taste like that of vinegar.

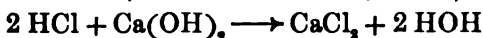
2. **Action on colored compounds.** Hydrochloric acid acts upon many colored compounds, changing the color in some way—very often to a red. Thus it readily changes the blue color of the compounds known as *litmus* to red.

3. *Action upon metals.* Many of the metals, such as sodium, iron, tin, and zinc, readily dissolve in hydrochloric acid, forming chlorides of the metals and liberating hydrogen :

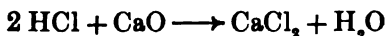


It will be recalled that this reaction is sometimes used for the preparation of hydrogen.

4. *Action upon the hydroxides of the metals.* When hydrochloric acid and a metal hydroxide are brought together, the hydrogen of the acid and the metal of the hydroxide exchange places, forming a chloride of the metal and water :



Similarly, the acid acts upon the oxides of the metals :



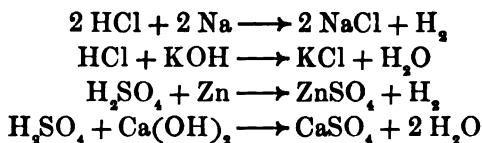
**Acids.** Hydrochloric acid is one of a large number of compounds known collectively as *acids*. Thus we have sulfuric acid, which is an aqueous solution of the compound  $\text{H}_2\text{SO}_4$ , called hydrogen sulfate ; nitric acid, which is hydrogen nitrate ( $\text{HNO}_3$ ) dissolved in water ; and acetic acid, present in vinegar. The properties of the acids are in general those described as belonging to hydrochloric acid. An acid may therefore be defined as a *compound whose aqueous solution (1) has a sour taste ; (2) changes blue litmus to red ; (3) dissolves certain metals, liberating hydrogen, and (4) reacts with metallic hydroxides, the hydrogen of the acid exchanging places with the metal of the hydroxide.* Acids change the color not only of litmus but of many other colored substances. Such substances may be used to detect the presence of an acid and when so used are called *indicators*.

In addition to the above properties held in common, acids have other properties, which may vary widely in different cases. Thus, even dilute hydrochloric and sulfuric acids are poisonous

and entirely different in this respect from such acids as acetic acid (which is present in vinegar), citric acid (present in lemons), and malic acid (present in apples and pears).

**Basicity of acids.** The formulas of the three acids, hydrochloric ( $\text{HCl}$ ), sulfuric ( $\text{H}_2\text{SO}_4$ ), and phosphoric ( $\text{H}_3\text{PO}_4$ ), show that in one molecule there may be several hydrogen atoms. Experiment proves that all of them may be replaced by metals. The number of replaceable hydrogen atoms in a molecule of an acid is called the *basicity* of the acid, and an acid is said to be *monobasic*, *dibasic*, or *tribasic*, according to whether it has in each molecule one, two, or three atoms of hydrogen replaceable by metals. Hydrochloric acid is therefore monobasic, sulfuric acid is dibasic, and phosphoric acid is tribasic. The formulas of some acids, such as acetic ( $\text{C}_2\text{H}_4\text{O}_2$ ) and tartaric ( $\text{C}_4\text{H}_4\text{O}_6$ ), would apparently indicate a still higher basicity, but experiment shows that in the former only one hydrogen atom, and in the latter two, may be replaced by metals. On this account the formulas are usually written  $\text{H} \cdot \text{C}_2\text{H}_3\text{O}_2$  and  $\text{H}_2 \cdot \text{C}_4\text{H}_2\text{O}_6$ .

**Salts.** It has been pointed out that when an acid acts upon a metal or a metal hydroxide, the metal takes the place of the hydrogen in the acid. The resulting compound therefore differs in composition from the acid from which it is formed in that it contains a metal in place of hydrogen. Such compounds are known as *salts*. The following equations will serve to illustrate the formation of salts and to indicate their composition:

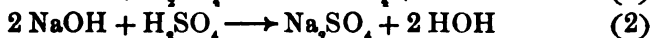


The compounds  $\text{NaCl}$  and  $\text{KCl}$  differ in composition from hydrochloric acid in that they contain the metals sodium and potassium in place of hydrogen and are therefore salts. Similarly, the compounds  $\text{ZnSO}_4$  and  $\text{CaSO}_4$  are salts derived from sulfuric acid.

*A salt may therefore be defined as a compound derived from an acid by replacing the hydrogen of the acid by a metal.*

It is evident that a number of salts can be formed from each acid; indeed, we might expect each acid to form as many salts as there are metals. This is not true, however, since some of the compounds are unstable and impossible to prepare. Nevertheless the number of salts is very large.

**Acid salts and normal salts.** If an acid contains more than one atom of hydrogen in the molecule, it is possible to replace either a part or all of the hydrogen atoms by a metal, as indicated in the following equations:



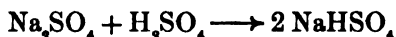
The compounds formed, namely  $\text{NaHSO}_4$  and  $\text{Na}_2\text{SO}_4$ , are both salts, since they both may be regarded as derived from sulfuric acid by replacing the hydrogen of the acid by a metal. In the one compound ( $\text{NaHSO}_4$ ), however, only a part of the hydrogen has been replaced, while in the other compound ( $\text{Na}_2\text{SO}_4$ ), all the hydrogen of the acid has been replaced. To distinguish between these two classes of salts, the former are called *acid salts* and the latter *normal salts*. This distinction may be stated more fully as follows:

*A salt is a compound derived from an acid by replacing the hydrogen of the acid by a metal. If only a part of the hydrogen is replaced, the resulting salt is called an acid salt; if all the hydrogen is replaced, then the salt is called a normal salt.*

The term *acid salt* is appropriate because such salts contain the constituents of both an acid and a salt. Thus the acid salt  $\text{NaHSO}_4$  contains the constituents H and the radical  $\text{SO}_4$ , in which respect it resembles sulfuric acid, and also Na and  $\text{SO}_4$ , the two constituents of sodium sulfate. In a general way these compounds have the properties of both an acid and a salt, although these properties may vary widely in different acid salts, as we shall note from time to time.

**Preparation of acid salts.** These salts may be prepared according to equation (1) above. They may also be prepared by

treating the normal salt with the corresponding acid, as indicated in the following equation :



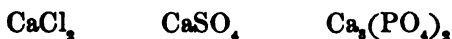
**Formulas of salts.** Knowing the valence of a metal and the formula of any acid, it is easy to deduce the formula of the salt which the metal may naturally be expected to form with the acid. Thus, suppose we wish to determine the formula of the salt which the element calcium forms with the acids  $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$ , and  $\text{H}_3\text{PO}_4$  respectively. First write the symbol of the element in place of the hydrogen of the acid :



Now write over the symbols of calcium, chlorine, and each of the radicals  $\text{SO}_4$  and  $\text{PO}_4$  the valence of each element or radical. ( $\text{SO}_4$  is bivalent, since it combines with 2 atoms of hydrogen ( $\text{H}_2\text{SO}_4$ ), while the radical  $\text{PO}_4$  is trivalent, since it combines with 3 atoms of hydrogen, as shown by the formula  $\text{H}_3\text{PO}_4$ .)



Finally, take such numbers of the two constituents of each salt as will add up an equal number of valences. This gives the following as the correct formulas :



**The naming of acids.** Acids containing but two elements like  $\text{HCl}$  are called *binary acids*. These are given names formed by combining the prefix *hydro-* with the name of the second element (abbreviated, if necessary, for the sake of euphony) and the termination *-ic*. Thus  $\text{HCl}$  is named hydrochloric acid,  $\text{HBr}$ , hydrobromic acid, and  $\text{H}_2\text{S}$ , hydrosulfuric acid.

In addition to the two elements present in binary acids, most acids contain oxygen. These are called *ternary*, or *oxygen acids*. Since all the oxygen acids contain both hydrogen and oxygen, the name of the third element is the one selected for designating the acid. Thus, in the acid  $\text{HNO}_3$ , it is nitrogen which gives its

name to the acid (nitric acid), while in the acid  $\text{H}_2\text{SO}_4$  it is the sulfur (sulfuric acid).

Often two or more acids are known which differ only in the percentages of oxygen present. Thus we have the acids  $\text{H}_2\text{SO}_3$  and  $\text{H}_2\text{SO}_4$ ;  $\text{HNO}_2$  and  $\text{HNO}_3$ . In such cases the most common of the group is given the termination *-ic*, while the one containing one less atom of oxygen is given the termination *-ous*; thus  $\text{HNO}_2$  is named *nitric acid*, while  $\text{HNO}_3$  is named *nitrous acid*. Similarly, we have *sulfuric acid* ( $\text{H}_2\text{SO}_4$ ) and *sulfurous acid* ( $\text{H}_2\text{SO}_3$ ). If an acid exists which has more oxygen than the *-ic* acid, it is named by prefixing the term *per-* (signifying "more") to the name of the *-ic* acid, while an acid containing less oxygen than the *-ous* acid is distinguished by the prefix *hypo-* (signifying "less"). Thus we have the acids  $\text{HClO}$ ,  $\text{HClO}_2$ ,  $\text{HClO}_3$ , and  $\text{HClO}_4$ , named respectively hypochlorous acid, chlorous acid, chloric acid, and perchloric acid.

**The naming of salts.** Binary salts are named by combining the names of the two elements present, using the termination *-ide*. Thus  $\text{NaCl}$  is sodium chloride and  $\text{KBr}$  is potassium bromide. Sometimes we have two binary salts containing the same elements. These are distinguished from each other by the terminations *-ous* and *-ic* added to the name of the metal, the *-ous* compound designating the one containing the largest percentage of the metal; thus  $\text{HgCl}$  and  $\text{HgCl}_2$  are called mercurous chloride and mercuric chloride respectively.

The names of ternary salts are derived from the names of the corresponding acids by changing the termination *-ic* of the acid to *-ate*, or if it is an *-ous* acid by changing the termination *-ous* to *-ite*, and in either case prefixing the name of the metal. The following examples will serve as illustrations:

ACID		SODIUM SALT
Hypochlorous . . . . .	$\text{HClO}$	Sodium hypochlorite . . . $\text{NaClO}$
Chlorous . . . . .	$\text{HClO}_2$	Sodium chlorite . . . $\text{NaClO}_2$
Chloric . . . . .	$\text{HClO}_3$	Sodium chlorate . . . $\text{NaClO}_3$
Perchloric . . . . .	$\text{HClO}_4$	Sodium perchlorate . . . $\text{NaClO}_4$

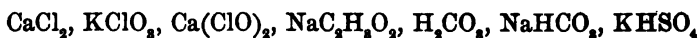
Acid salts are named like normal salts except that the word *hydrogen* is also used; thus  $\text{NaHSO}_4$  is called sodium hydrogen sulfate. Such salts are also often given the name of the normal salt with the prefix *bi-*; thus  $\text{NaHSO}_4$  is often called sodium bisulfate. The name *sodium acid sulfate* is also sometimes used.

**Salts of hydrochloric acid; the chlorides.** In connection with the study of hydrochloric acid it may be stated that its salts, known as the *chlorides*, constitute a very important group of compounds. Some of them, as sodium chloride and potassium chloride, are found in nature. A number of the metals, including copper, mercury, and tin, combine with different percentages of chlorine, and thus form two chlorides. Nearly all the chlorides of the metals are solids and, with the exception of those of silver, mercury (mercurous), and lead, the chlorides of all the common metals are soluble in water.

Some of the more important chlorides are the following: sodium chloride (salt) ( $\text{NaCl}$ ); potassium chloride ( $\text{KCl}$ ); mercurous chloride (calomel) ( $\text{HgCl}$ ); mercuric chloride (corrosive sublimate) ( $\text{HgCl}_2$ ); ferric chloride ( $\text{FeCl}_3$ ); barium chloride ( $\text{BaCl}_2$ ); calcium chloride ( $\text{CaCl}_2$ ).

### QUESTIONS

1. Contrast the physical properties of the elements so far studied.
2. Distinguish between the terms *catalysis* and *electrolysis*.
3. Chlorine acts upon ammonia ( $\text{NH}_3$ ) to form hydrogen chloride and nitrogen. Write the equation for the reactions, indicating the steps taken to balance the equation.
4. Suggest a reason why chlorine does not bleach printer's ink.
5. Distinguish clearly between the following classes of compounds, giving one or more examples to illustrate each: acids, salts, acid salts, normal salts, monobasic acid, tribasic acid.
6. Designate the class to which each of the compounds represented by the following formulas belongs, and give the name of each of the compounds:



7. The metals potassium, barium, and aluminium have a valence of 1, 2, and 3 respectively; write the formulas of the normal salts which you would expect each of these metals to form with the following acids:  $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{H}_3\text{PO}_4$ .

#### PROBLEMS

1. Which would yield the greater amount of chlorine when heated with hydrochloric acid, 100 g. of manganese dioxide or 100 g. of potassium permanganate?

2. A certain chlorine plant produces 20 tons of chlorine daily. Calculate the weight of sodium chloride used daily, as well as the weights of the various products resulting from the electrolysis of the salt.

3. The concentrated hydrochloric acid of commerce has a density of approximately 1.20 and contains 40 per cent of hydrogen chloride. What weights of raw materials are necessary for the production of 100 kg. of this acid?

4. Calculate the weights of the by-products formed in Problem 2.

5. A compound was found by analysis to have the following composition: Mn, 36.38 per cent; S, 21.23 per cent; O, 42.39 per cent. Calculate the formula of the compound.

## CHAPTER XIV

### SODIUM; SODIUM HYDROXIDE; BASES

**Introduction.** The elements so far discussed all belong to the group known as *nonmetals*. It is desirable at this point to discuss somewhat in detail a typical *metal*, and the one that best serves our purpose is *sodium*. Reference has been made to this metal in connection with the preparation of hydrogen (p. 44), while some of its compounds, such as sodium chloride, have often been mentioned.

**History.** The isolation of sodium dates back to the year 1807. At that time the compounds now known as sodium hydroxide and potassium hydroxide were well known and were called *fixed alkalies*, but they were regarded as elementary in character. In 1807 Sir Humphry Davy, while studying the effect of the electric current upon various substances, succeeded in decomposing these fixed alkalies and obtained metallic sodium and potassium.

Davy announced his discovery in a letter to a friend, as follows: "I have decomposed and recomposed the fixed alkalies and discovered their bases to be two new inflammable substances very like metals; but one of them lighter than ether and infinitely combustible. So that there are two bodies decomposed and two new elementary bodies found."

**Occurrence.** Because of its very great activity, especially toward water, sodium does not occur free in nature, but its compounds are abundant. Its compounds with silicon and oxygen, known as silicates, are found in many igneous rocks, especially in the feldspar known as albite. By the disintegration of these rocks compounds of sodium pass into the soil, from which they are taken up by plants, although not in such large quantities as are potassium compounds. The most familiar compound of sodium is the chloride which occurs in all salt and mineral waters

and also forms large deposits in various parts of the world. Other sodium compounds found in nature are the nitrate (Chile salt-peter), the carbonate, the sulfate, and the borate (borax).

**Preparation.** For many years the most economical method known for preparing sodium consisted in the reduction of its carbonate:



At present it is all prepared by the electrolysis of either the fused hydroxide or chloride. It is evident that all water must be excluded in the process; otherwise the sodium liberated will react with the water and form sodium hydroxide.

**Castner's process.** At Niagara Falls sodium is prepared by passing a current of electricity through fused sodium hydroxide by a process devised by Castner. The apparatus consists of a cylindrical iron vessel *A, A* (Fig. 74), through the bottom of which extends an iron rod *B*, which serves as the cathode. The iron anodes *C, C*, several in number, are suspended around the cathode but are kept from touching it by a cylinder of iron gauze *D*, which is fastened to the vessel *E*. The lower part of the vessel *A, A* is filled with melted sodium hydroxide, which, on cooling, holds the cathode in position. The heat generated by the current is ordinarily sufficient to keep the hydroxide in the upper portion of the vessel fused; however, the apparatus is supplied with a row of gas burners *G, G*, which may be utilized if additional heat is required. Sodium and hydrogen are liberated at the cathode and, rising to the surface, collect in the vessel *E*. The hydrogen escapes by lifting the cover of the vessel, while the sodium, protected from the air by the hydrogen, is skimmed or drawn off from time to time. Oxygen is liberated at the anodes and escapes through the opening *F* without coming in contact with either the sodium or the hydrogen.

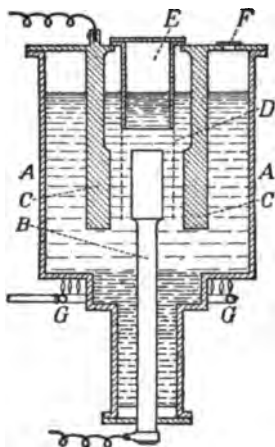


FIG. 74

**Properties and uses.** Sodium is a soft, silver-white metal, slightly lighter than water. It melts at  $97.5^{\circ}$  and boils at  $877^{\circ}$ . It is very active chemically, combining readily with most of the nonmetallic elements such as oxygen and the halogens.

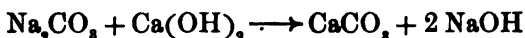
It decomposes water and reacts with acids, forming the corresponding salts and liberating hydrogen. It dissolves in mercury, forming an alloy (sodium amalgam) which is an efficient reducing agent. When heated in the Bunsen flame, sodium, as well as most of its compounds, volatilizes and imparts a yellow color to the flame, — a property which is used as a test for the presence of the element.

Sodium is used in the preparation of sodium cyanide and sodium peroxide and to a limited extent as a reducing agent. It is also used in the preparation of the well-known dye, indigo.

**Compounds of sodium.** Sodium forms many useful compounds. One of these, sodium hydroxide, is a typical member of that important class of compounds known as *bases*, and it is desirable for us to study its properties at this time; the discussion of the other compounds of sodium may well be deferred to a later chapter.

**Sodium hydroxide (caustic soda) ( $\text{NaOH}$ ).** This compound is prepared on a large scale by two general processes.

1. *Action of calcium hydroxide upon sodium carbonate.* This process consists in treating calcium hydroxide suspended in water with sodium carbonate ( $\text{Na}_2\text{CO}_3$ ). Calcium carbonate, being insoluble, is precipitated:



The resulting sodium hydroxide is obtained by filtering off the calcium carbonate and evaporating the filtrate to dryness.

While this is an old process it still remains the chief one for the production of the hydroxide. Manufacturers of sodium carbonate often utilize a portion of their product in the preparation of the hydroxide, so that the manufacture of these two compounds is often carried out in the same plant.

2. *Electrolytic methods.* In connection with the electrolytic preparation of chlorine (p. 195) it was stated that when an electrical current is passed through a solution of sodium chloride, both chlorine and sodium hydroxide are produced, the former escaping as a gas. Not all the sodium chloride is decomposed, so

that the resulting solution contains both sodium chloride and sodium hydroxide. The chloride is much less soluble than the hydroxide, so that when the solution is partially evaporated, the chloride separates, leaving a nearly pure solution of hydroxide. This is then evaporated to dryness, and the sodium hydroxide is fused to drive off all the water. As it cools, the product solidifies in the form of a white solid and in this form is sold on the market.

The product as prepared by either of the above methods is never pure. If desired, it may be further purified by treatment with alcohol, which dissolves the sodium hydroxide but only small amounts of the impurities present. Perfectly pure sodium hydroxide may best be obtained by dissolving sodium in water and evaporating the resulting solution.

**Properties of sodium hydroxide.** This compound is a white crystalline, brittle solid. For laboratory purposes it is ordinarily sold in the form of sticks, in shape resembling sticks of candy. When exposed to the air, it absorbs both moisture and carbon dioxide and is changed into sodium carbonate ( $\text{Na}_2\text{CO}_3$ ). It is often called *caustic soda*. As this name indicates, it is a corrosive substance and has a strong disintegrating action upon both animal and vegetable tissues. Its solution has a soapy feel and a strong cleansing action.

Sodium hydroxide has certain properties in common with the hydroxides of the other metals. These common properties are as follows:

1. **Action on coloring matter.** Its action on coloring matter is just the opposite of that of the acids; for example, it turns the color of litmus from red to blue.

2. **Action upon acids.** It reacts with acids to form salts and water as already explained (p. 206).

**Uses of sodium hydroxide.** The compound is used in many chemical industries. Some idea of its importance can be judged from the fact that it is used in the manufacture of all hard soaps. If, as is sometimes stated, the state of civilization of a country can be told by the amount of soap it consumes, then the same

statement will hold for the amount of caustic soda used. The compound is also used in the refining of kerosene and other oils and in the manufacture of paper. Under the name of *lye* it is sold as a household article for cleansing purposes.

**Significance of the terms *commercial* and *chemically pure*.** Most compounds when prepared on a large scale contain varying amounts of impurities consisting of the substances used in the preparation of the compounds. In this form compounds are designated by the term *commercial*. Thus we have commercial sodium hydroxide which may contain 10 per cent or more of other ingredients. For many of the uses of compounds the presence of a limited percentage of impurities makes no difference, and for such purposes the commercial forms are used since they are much cheaper. On the other hand, certain uses require a pure substance, and this necessitates the removal of the impurities, which is oftentimes an expensive process, considerably increasing the cost of the final product. The compounds so purified are known as *chemically pure*, or simply as *C. P.*, to distinguish them from the commercial product.

**Bases; alkalis.** Sodium hydroxide is one of a group of compounds, each member of which consists of a metal combined with oxygen and hydrogen. Thus we have  $\text{NaOH}$ ,  $\text{KOH}$ ,  $\text{Ca}(\text{OH})_2$ , and  $\text{Al}(\text{OH})_3$ . The  $\text{OH}$  group in these compounds acts as a radical and has the name *hydroxyl*. These compounds are known collectively as the *bases*. Like the acids, their basic properties are only developed in the presence of water. Accordingly we may define a base as follows: *A base is a compound containing a metal and one or more hydroxyl groups. In the presence of water it changes the color of litmus from red to blue and reacts with acids to form salts and water.*

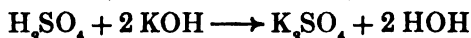
Those hydroxides which have the most highly developed basic properties are often called *alkalis*. The common alkalis are sodium hydroxide, potassium hydroxide, and calcium hydroxide.

**Acidity of bases.** The formulas for potassium hydroxide ( $\text{KOH}$ ), for calcium hydroxide ( $\text{Ca}(\text{OH})_2$ ), and for aluminium hydroxide ( $\text{Al}(\text{OH})_3$ ) show that molecules of bases may contain more than one hydroxyl group. When the molecule contains but one hydroxyl group, the base is said to be a *monacid* base; when

two, a *diacid* base; when three, a *triacid* base. There are a few tetracid bases, such as stannic hydroxide ( $\text{Sn}(\text{OH})_4$ ), but for the most part these lose a molecule of water and act as diacid bases:



**Neutralization.** When an acid and a base are brought together, a reaction takes place which consists in the interchange of the hydrogen of the acid and the metal of the base, forming a salt and water, thus:



This interaction of an acid and a base to form a salt and water is known as *neutralization*, and the acid and base are said to *neutralize* each other in the process. It is evident from the above equations that both the acid and the base disappear as such in the reaction, and in their places we have a salt and water. By the evaporation of the water the salt may be obtained in pure form. Neutralization therefore serves as a general method for the preparation of salts.

**Neutralization a definite act.** If two solutions, one of a base and the other of an acid, are prepared, experiment has shown that a given volume of the acid will invariably require a perfectly definite volume of the base for its neutralization.

The experiment is most easily performed with the aid of burettes (Fig. 75), which are graduated tubes furnished with a stopcock at one end. The one is filled to the zero mark with the acid solution, the other with the basic. A measured volume of the one solution is drawn off into a small beaker, a few drops of an appropriate indicator added, and the second solution run in with constant stirring until the indicator just turns color. If the concentration

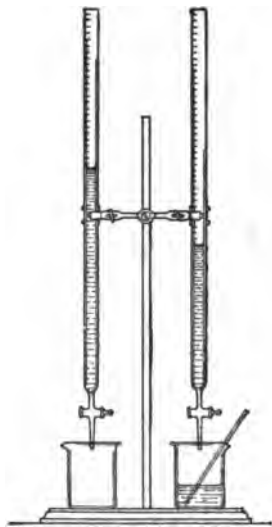
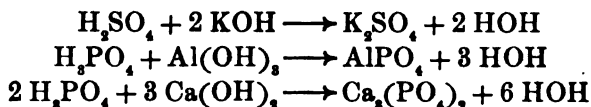


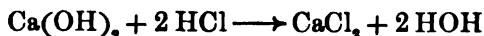
FIG. 75

of each solution is accurately known, it is easy to calculate, from the volumes required for neutralization, the ratio by weight between the acid and the base taking part in the action. Experiment shows that this ratio always bears a simple relation to that between the molecular weights of the reacting substances. Such a reaction as is indicated in the equation  $\text{NaOH} + \text{HCl} \longrightarrow \text{NaCl} + \text{H}_2\text{O}$  is, therefore, perfectly definite, and if we know the weight of an acid employed, we can calculate the weight of the base required to neutralize the acid and also the weight of the salt formed.

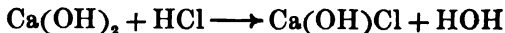
**Balancing equations of neutralization.** It will be noted that in the equations representing neutralization the hydrogen of the acid replaced by the metal combines with the hydroxyl group of the base to form water. Both the hydrogen atom and the hydroxyl radical are univalent and therefore combine in the ratio of one to one. Accordingly, in balancing an equation that represents neutralization it is necessary to take the acid and the base in such proportions that the number of hydrogen atoms of the acid is the same as the number of hydroxyl radicals of the base, thus:



**Basic salts.** When a base containing more than one hydroxyl group, as  $\text{Ca}(\text{OH})_2$ , reacts with a monobasic acid such as hydrochloric acid, two molecules of the acid are required to neutralize one molecule of the base:



If the base and acid are mixed in the ratio of one molecule of each, then the neutralization is not complete:



The resulting compound,  $\text{Ca}(\text{OH})\text{Cl}$ , has present in it the constituents of a base, namely, Ca and OH, but it also has the constituents of a salt, Ca and Cl. The compound is therefore called a *basic salt*. *A basic salt may be defined as a compound which contains the constituents of both a base and a salt.*

**Normal solutions.** In scientific investigation, as well as in industrial analysis, it is often desirable to estimate the weight of acid or base in a given volume of solution. For example, the acid in vinegar and the alkali in lye or limewater must be determined very frequently. This may be readily accomplished by neutralizing the solution of unknown concentration with a solution of an acid or a base the concentration of which is accurately known, as explained under Fig. 75. Such a solution is called a *standard* solution. The standard may be of any convenient concentration, depending upon the character of the solutions to be investigated. If the standard solution of an acid is prepared in such a way that 1 l. will contain 1 g. atomic weight of hydrogen (1.008 g.), then it is said to be a *normal solution*. Similarly, a normal solution of a base is one that contains 17.008 g. (1.008 + 16) of the radical OH in 1 l. Solutions half this concentration are said to be half-normal (N/2). Tenth-normal solutions (N/10) are still more frequently employed.

In order to prepare a normal solution of a monobasic acid such as hydrochloric acid, it is evident that one must have present in each liter of the solution 1 g. molecular weight of the acid, since this amount would contain 1.008 g. of hydrogen. Thus a normal solution of hydrochloric acid will contain 36.468 g. (1.008 g. H + 35.46 g. Cl) of hydrogen chloride. With dibasic acids, on the other hand, 1 l. of the normal solution will contain only half the gram-molecular weight of the acid. The same general principles hold in the preparation of normal alkaline solutions.

Such solutions greatly simplify calculations, for it is evident that 1 l. of a normal solution of any acid will neutralize 1 molar weight of any monacid base; 10 cc. will neutralize  $\frac{1}{10}$  of its molar weight. If in neutralizing a solution of lye (NaOH) of unknown concentration 20 cc. of normal acid is required, then the solution of lye contains  $\frac{20}{1000} \times 40.01 (= 0.8002)$  g. NaOH.

### QUESTIONS

1. From the method of preparation, what impurities would you expect to find in commercial sodium hydroxide?
2. Name the following compounds and designate the class (acid, base, salt) to which each belongs:  $\text{Ca}(\text{OH})_2$ ,  $\text{SnCl}_2$ ,  $\text{SnCl}_4$ ,  $\text{PbBr}_2$ ,  $\text{H}_4\text{SiO}_4$ ,  $\text{KClO}_4$ .

3. Contrast the composition and properties of acids and bases.
4. Acids in contact with cloth often change the color of the dye used in coloring the cloth. Suggest a possible method of restoring the color.
5. Write the equations for the reactions which take place when aluminium hydroxide ( $\text{Al}(\text{OH})_3$ ) is neutralized by each of the following acids:  $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$ . Name each of the compounds formed.
6. Write the equations for the reactions that take place in the preparation of the following salts by the method of neutralization: aluminium nitrate ( $\text{Al}(\text{NO}_3)_3$ ), magnesium sulfate ( $\text{MgSO}_4$ ), chromium sulfate ( $\text{Cr}_2(\text{SO}_4)_3$ ), zinc chloride ( $\text{ZnCl}_2$ ).

### PROBLEMS

1. Suppose you wish to prepare 100 kg. of aluminium sulfate. What compounds and what amounts of each would be required for preparing it by the method of neutralization?
2. The Government chlorine plant built during the war had a capacity of 100 tons of chlorine daily. What was the daily output of sodium hydroxide when the plant ran at full capacity?
3. In what proportions must hydrochloric acid and sodium hydroxide be mixed in order to effect complete neutralization?
4. What weights of each of the following compounds will be required to prepare 1 l. of a normal solution of each:  $\text{NaOH}$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{H}_3\text{PO}_4$ ,  $\text{Ca}(\text{OH})_2$ ?
5. 25 cc. of a normal solution of sodium hydroxide was required to neutralize the acid present in 5 cc. of a sample of sulfuric acid. What is the strength of the acid in terms of grams in 1 l.?

## CHAPTER XV

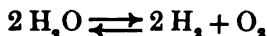
### IONIZATION

**Introduction.** In Chapter XII it was shown that the effect produced upon such properties of a solvent as the boiling and freezing points, the vapor pressure, and the osmotic pressure depends upon the ratio of the *number of molecules of the solute to that of the solvent* and not upon the specific chemical properties of either one; just as gas pressure depends upon the number and not the kind of molecules present. The fact has been emphasized that *acids, bases, and salts (or, in general, electrolytes) do not exhibit these regularities* but give abnormal results.

**Irregularities in solutions of electrolytes.** When an acid, a base, or a salt is dissolved in water, the effect produced upon the freezing or boiling point or the vapor pressure of the water, and also the osmotic pressure of the solution, *is greater* than that calculated from the laws that hold true for nonelectrolytes. The deviation from the calculated effect varies between wide limits. With some electrolytes the excess is slight; with others it reaches a double or even triple value. *Moreover, it varies with the concentration, being relatively greater in dilute solutions than in more concentrated ones.* The table on page 222 shows the effects produced upon the freezing point of water by a typical salt, base, and acid when compared with that produced by alcohol, which is not an electrolyte.

If the conclusion reached in the study of nonelectrolytes is correct, — namely, that it is the *relative number of molecules* of the solute, not its character, which determines the effect, — then in the case of electrolytes the thought occurs, May it not be that, when dissolved in water, *electrolytes undergo a dissociation*

into units smaller than molecules, which therefore increases the number of independent particles? We are familiar with such a dissociation occasioned by heat. It will be remembered that at high temperatures water dissociates to some extent, setting up the equilibrium represented in the equation



the number of independent units increasing from 2 to 3 in so far as the reaction proceeds, and the gas pressure increasing correspondingly. We shall first seek for evidence that there is a somewhat similar dissociation in solutions of electrolytes, and then endeavor to form a theory as to its character.

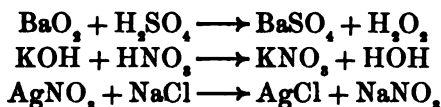
**Evidence for dissociation in solutions of electrolytes.** There are a number of lines of evidence which may be mentioned in support of the view that in solutions of electrolytes a dissociation takes place.

#### LOWERING OF THE FREEZING POINT OF WATER

SUBSTANCE	CHARACTER	FORMULA	LOWERING PRODUCED IN 1000 CC. OF WATER BY 1 GRAM-MOLECULE OF SUBSTANCE
Alcohol . . . . .	nonelectrolyte	$\text{C}_2\text{H}_5\text{O}$	1.872
Hydrogen chloride . . .	acid (electrolyte)	HCl	3.806
Hydrogen nitrate . . .	acid (electrolyte)	$\text{HNO}_3$	4.100
Potassium hydroxide . .	base (electrolyte)	KOH	3.773
Sodium hydroxide . . .	base (electrolyte)	NaOH	3.465
Sodium chloride . . . .	salt (electrolyte)	NaCl	3.546
Potassium nitrate . . .	salt (electrolyte)	$\text{KNO}_3$	2.729

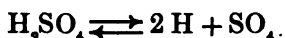
1. **Abnormal constants of solutions of electrolytes.** The fact of the excessive effect produced by electrolytes on the lowering of the freezing point and vapor pressure, on the raising of the boiling point, and on the magnitude of osmotic pressure is evidence pointing toward the increase in number of independent units in solution, provided our conclusions in regard to nonelectrolytes are justified.

2. *Chemical reactions of solutions of electrolytes.* There is a simplicity in the chemical action of electrolytes upon each other in solution which is strongly suggestive of the presence of dissociated products. The prevailing type of reaction in their solutions is illustrated by such equations as the following:



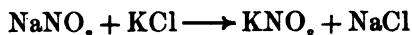
It will be seen that these reactions express a simple interchange, the metals exchanging places with each other or with hydrogen, while such radicals as  $\text{SO}_4$  and  $\text{NO}_3$  go through the reaction as units. Moreover, the reactions proceed with great rapidity, indicating that little preliminary work is involved in decomposing the materials into these radicals. This is very different from most of the reactions of nonelectrolytes in solution, which are slow, or from those occasioned by heat, such as the decomposition of potassium chlorate, the course of which in general cannot be predicted at all.

It would appear that with electrolytes there is a distinct line of weakness in the molecule—that sulfuric acid tends to part into hydrogen and the radical  $\text{SO}_4$  with great ease, while the radical  $\text{SO}_4$  tends to act as a unit. This suggests that in solution the acid may really be in the condition represented by the equilibrium equation



3. *The law of thermoneutrality.* It has long been known that when dilute solutions of two soluble salts are mixed there is little or no heat change, this generalization being known as the *law of thermoneutrality*. It states a singular fact, for in many such cases chemical action undoubtedly takes place and we expect this to be accompanied by heat changes. Thus, when dilute solutions of sodium nitrate ( $\text{NaNO}_3$ ) and potassium chloride ( $\text{KCl}$ ) are mixed, there is no heat change. On evaporation a

certain quantity of potassium nitrate ( $\text{KNO}_3$ ) and sodium chloride ( $\text{NaCl}$ ) is obtained, showing that the reaction expressed in the following equation has, at least to some extent, taken place :



If in dilute solution the various molecules represented in the equation are all parted into the independent units  $\text{K}$ ,  $\text{Na}$ ,  $\text{Cl}$ ,  $\text{NO}_3$ , and only in concentrated solution form any considerable number of molecules, we can see why there should be little evidence of reaction on mixing the dilute solutions, although in concentrated solution action takes place accompanied by heat changes.

4. *The facts of electrolysis.* We owe much of our knowledge as well as many of our definitions connected with electrolysis to the Englishman Michael Faraday, who made his largest contributions

to the subject in the third decade of the last century.

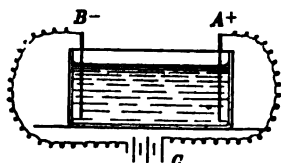


FIG. 76

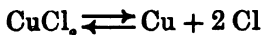
A substance whose solution will conduct the current is termed an *electrolyte*. The electrolyte is always decomposed during the passage of the current, and the process of decomposition is called

*electrolysis*. The plates dipping into the solution (Fig. 76) are called the *electrodes*,—the positive plate *A*, by which the current is said to enter, being the *anode*, and the negative *B*, by which it leaves, the *cathode*. The battery generating the current is represented by *C*. The passage of the current is attended by the movement of dissolved particles through the solvent toward the two electrodes, and it is by means of this movement that the current is carried. The moving particles are called *ions*, from the Greek word meaning "to go," those moving toward the anode being termed *anions*, and those moving toward the cathode, *cations*. During electrolysis, decomposition products of the electrolyte are deposited on the electrodes or concentrate about them. For example, when copper chloride ( $\text{CuCl}_2$ ) undergoes electrolysis, the copper is deposited on the cathode, while the

chlorine is set free at the anode, the products thus appearing at places which may be far apart.

Now Faraday found that when one gram-atomic weight of *any univalent metal* (or hydrogen) has been liberated at the cathode, a *definite quantity of electricity has been carried through the solution*, namely 96,540 coulombs. This generalization is known as Faraday's law, and the quantity 96,540 coulombs is called a *faraday*. The quantity of electricity depends, therefore, merely *on the number of univalent ions, not on their character*. In depositing a gram-atomic weight of a *bivalent* metal 2 faradays of current must pass through the solution. The atomic weight of an element divided by its valence is called the *electrical equivalent* of the element. To deposit the electrical equivalent of any element requires 1 faraday of current. Moreover, under properly chosen conditions it can be shown that very little electrical energy is absorbed in the decomposition of the salt.

All these facts — the appearance of the products of decomposition at distant electrodes, the equal quantities of electricity which an equivalent of every metal carries, the fact that under properly chosen conditions there is no absorption of energy due to decomposition of the electrolyte — suggest that *in the act of passing into solution* there is a decomposition of the electrolyte of the character represented in the equilibrium equation



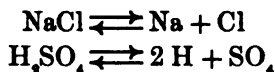
*and that the passage of the current does not cause decomposition but depends upon it.*

**Theory of ionization.** With the several laws relating to solutions of electrolytes and electrolysis as a foundation, the Swedish chemist Arrhenius, in 1887, put forward a theory of solutions of electrolytes which has come to be known as the *theory of ionization*. The chief points of this theory are as follows:

1. *Electrolytes form ions in solution.* When electrolytes are dissolved in water, their molecules tend to part into two kinds of atoms, or groups of atoms, which Arrhenius termed *ions*,

following Faraday's usage. Faraday formed no precise hypothesis in regard to the nature of the electrical carriers in solution, but Arrhenius made the definite assumption that they are not the same as molecules but are formed by their decomposition.

2. *The ionization of the electrolyte results in an equilibrium.* The molecules of the electrolyte do not all so break down, for if they did, an electrolyte would have *just twice* the effect upon the physical constants of a solvent that a nonelectrolyte has. An equilibrium is presently reached between the molecules decomposing into ions and those forming again from the ions. In the case of sodium chloride and sulfuric acid, for example, this may be expressed by the equilibrium equations



3. *Various factors which influence the equilibrium.* The point at which equilibrium is reached depends largely upon three things:

(a) *The nature of the electrolyte.* Electrolytes show great differences among themselves as to the extent to which they give abnormal physical constants or conduct the current. This is assumed to indicate a varying percentage of ionization.

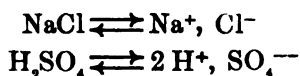
(b) *The nature of the solvent.* This has much influence upon the ionization, many solvents, such as ether and benzene, producing none at all, and others, such as liquid ammonia and sulfur dioxide, showing the same effects as water, but each to a different degree.

(c) *The dilution.* As the solution becomes more dilute, a larger percentage of the solute is ionized. From a kinetic standpoint this is entirely reasonable, for the more widely the ions are scattered through a solution the less frequently they will have opportunity to recombine; so the equilibrium will move steadily toward a larger proportion of ions as the dilution increases.

4. *The ions are electrically charged.* The theory must include some explanation of the way in which the ions differ from ordinary molecules and atoms. The equilibrium equation



does not express the whole truth; for we know that sodium decomposes water violently, and chlorine is a gas but slightly soluble in water and possessing a very disagreeable odor; yet we also know that sodium chloride forms an odorless and perfectly stable solution. Arrhenius considers that these differences may be accounted for if we assume that *the ions are heavily charged with electricity*, and that in consequence of such charges they have totally different properties from the uncharged atoms and compounds. Each molecule, on ionizing, yields two kinds of ions, having equal and opposite charges as represented in the equations



Since the opposite charges are always equal, the solution as a whole remains electrically neutral. It is by virtue of these charges on movable bodies that the electrolyte conducts the current through a solution.

5. *Not all compounds ionize.* It is assumed that only those compounds ionize whose solutions are electrolytes. Thus salt ionizes when dissolved in water, for it has been found that the resulting solution is a very good electrolyte. Sugar, on the other hand, does not ionize, for its solution is not a conductor of the electric current.

**Apparatus.** Fig. 77 illustrates a very convenient apparatus for determining whether a solution is a good conductor. The solution is placed in the bottle *A* and the electrodes are

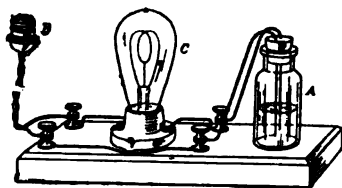


FIG. 77

dipped into it. Connection with the lighting circuit is made by the cord and plug *B*. If the solution is a good conductor, the current will flow through the lamp *C*, which will then glow.

**Source of the charges upon the ions.** The present state of advance in our knowledge of electricity makes it possible to form a more definite conception of the source of the charges

upon these ions. It appears to be certain that the atoms of the elements are not homogeneous bodies but are organized systems, each containing its own number of smaller bodies, which are called *electrons*. These electrons are all alike, and appear to be about  $\frac{1}{1845}$  the weight of a hydrogen atom. They can be separated from ordinary matter, so they are capable of existing in the free state. The evidence goes to show that the electrons are really atoms of electricity, which is therefore a material thing. A body containing more than its normal number of electrons is said to be negatively charged, while one from which some of its normal number of electrons have been removed is said to be positively charged. Electrical energy is the energy of innumerable electrons in very rapid motion.

Applying these views to the electrification of ions, we assume that before union the atoms of sodium and chlorine have each their normal number of electrons. When these combine to form solid sodium chloride, we have no definite knowledge as to any redistribution of the electrons in the several atoms. When the sodium chloride is dissolved in water, however, it appears that this distribution tends to change. *The sodium atom loses one electron and the chlorine gains one.* The sodium atom is now positively charged, the chlorine negatively, and in this condition they can part from each other to form independent ions. Upon recombination the original condition of the two atoms is restored, and the molecule is electrically neutral. The ions are therefore very different things from the atoms; they should even have different weights, though we cannot verify this experimentally.

In all probability it will appear confusing to the student to speak of an atom that has *lost* an electron as being *positively* charged, for in an algebraic sense a loss is represented as negative, not positive. He must remember that the terms *positive* and *negative* as applied to electricity have been in use so long, without any knowledge as to what electricity really is, that we cannot now reverse the two terms to make them harmonize with algebraic language as we should like to do if we could.

**Calculation of the percentage of ionization.** We have seen that in the case of nonelectrolytes a definite molar concentration always results in a

perfectly definite change in freezing point, boiling point, vapor pressure, and a definite osmotic pressure, irrespective of the properties of the solute. All these effects are greater at a given concentration in the case of an electrolyte. If, now, we compare the effect produced by an electrolyte with that produced by a nonelectrolyte at equal molar concentration, we can calculate the percentage of ionization that must have taken place to produce the larger effect.

Since the electrical conductivity of a solution depends upon the number of ions present to carry the current, we can also devise methods of calculation based upon the conductivity of a solution that will tell us the percentage of ionization that has occurred. It is evident that if all these methods of calculation should agree, within reasonable limits, we shall have a strong argument for the value of the theory we are forming. The following table gives a few figures to show the agreement between the results obtained by two of these methods:

DEGREE OF IONIZATION AS SHOWN BY TWO METHODS

COMPOUND SYMBOL	CONCENTRATION (MOLAR)	CALCULATED FROM FREEZING POINT	CALCULATED FROM CONDUCTIVITY
HCl	0.01	98.9	95.8
HCl	0.1	93.9	88.6
H <sub>2</sub> SO <sub>4</sub>	0.05	62.3	60.7
H <sub>2</sub> SO <sub>4</sub>	0.005	85.4	83.8
KOH	0.1	92.8	83.1
KOH	0.01	99.2	93.7
NaCl	0.1	84.1	84.1
NaCl	0.01	93.5	90.5
BaCl <sub>2</sub>	0.05	75.3	77.7
BaCl <sub>2</sub>	0.005	87.9	87.6
K <sub>2</sub> CO <sub>3</sub>	0.05	71.9	77.5
K <sub>2</sub> CO <sub>3</sub>	0.005	88.6	96.0

**Agreement between the methods.** It must be said that these methods do not always yield satisfactory agreement among themselves. When we remember the widely different conditions under which the experiments are made, — at the freezing point, at the boiling point, and at ordinary room temperature, — the lack of agreement is not surprising. Moreover, we know very little as to the extent to which chemical combination between solvent and solute enters in to complicate the matter. In general, there are so many complicating circumstances of which we are aware, and, doubtless, so many others of which we know nothing, that it may be said the methods agree as closely as could be expected.

**The atomic reality and the theory of ionization.** We have seen that what was formerly a theory of atoms has in time ceased to be regarded as a theory and is thought of as expressing a reality. The next step forward is to gain some insight into the structure of the various kinds of atoms, and the theory of ionization is a move in this direction. As yet we are not certain that the picture it presents is entirely satisfactory. This picture has already been considerably modified since it was first drawn, and will, no doubt, be further modified in the future. It has, however, stimulated a vast amount of research, has greatly extended our knowledge, and at the present time gives us by far the most satisfactory conception of solutions that we have. A great many of the facts of chemistry can be presented much more simply in terms of this theory than in any other way open to us at present. If we keep before us the limitations of all theory, we shall be able to use this one to great advantage.

### QUESTIONS

1. Define the terms *electrolyte*, *faraday*, *ion*, *electron*, *anode*, *cathode*.
2. In what processes have the terms *electrolysis* and *electrode* been employed in earlier chapters?
3. Suppose that on mixing two solutions a precipitate occurs. Would you expect the law of thermoneutrality to hold good?
4. In what respects does Faraday's law recall the law of multiple proportion?
5. What evidence does Faraday's law seem to suggest as to the nature of electricity?
6. What are the differences in properties between  $\text{Na}$  and  $\text{Na}^+$ ?
7. What would be the difference between the ions of iron derived from the salts  $\text{FeCl}_2$  and  $\text{FeCl}_3$ ?
8. Write the equations for the ionization of the following salts:  $\text{NaNO}_3$ ,  $\text{CaCl}_2$ ,  $\text{CaSO}_4$ ,  $\text{Al}_2(\text{SO}_4)_3$ .
9. Instead of assuming that the molecules of the solute dissociate, let us assume that the molecules of the solvent become double. Will this explain the abnormal conduct of the electrolyte?

**PROBLEMS**

1. If 1000 coulombs of electricity passes through a solution of a silver salt, what weight of silver will be deposited?
2. If 500 coulombs of electricity passes through a solution of copper sulfate, what weight of copper will be deposited?
3. How much current (in coulombs) will be required to deposit 100 g. of copper from a solution of  $\text{CuCl}$ ? from a solution of  $\text{CuSO}_4$ ?
4. So far as cost of current is concerned, what is the relative cost of depositing 1 g. of silver in silver-plating, as compared with that of depositing 1 g. of nickel in nickel-plating?

## CHAPTER XVI

### SOME APPLICATIONS OF THE THEORY OF IONIZATION

**Introduction.** Having formulated a theory of ionization primarily to account for the abnormal properties of electrolytes in solution, the next logical step is to see how far the theory is in accord with the large body of facts that are known in connection with the chemical conduct of solutions of electrolytes, and to find out whether the picture the theory presents helps us in understanding these facts.

**I. The theory of ionization and the facts of electrolysis.** Let us first get before us a few of the facts relating to the electrolysis of some solutions of familiar electrolytes and see how our theory fits in with these facts. This can be done best by some illustrative examples.

**Example 1. The electrolysis of sodium chloride.** Experiments show (p. 193) that when the electric current is passed through an aqueous solution of sodium chloride there are formed at



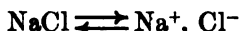
FIG. 78

the cathode sodium hydroxide, which remains in solution, and hydrogen, which is evolved as a gas. At the anode chlorine is set free and either escapes in the form of a gas or reacts with the constituents of the

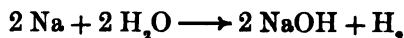
solution, according to the condition of the experiment.

In terms of the theory of ionization the interpretation of these facts is as follows: Let Fig. 78 represent a solution of sodium chloride, into which dip the electrodes *A* and *B*. The battery *C* keeps the anode charged positively and the cathode *B* negatively. In other words, it causes a drift of electrons through the wire

from *A* around to *B*, where they accumulate on the cathode, the anode being left deficient in them. Sodium chloride in solution ionizes in accordance with the equilibrium equation

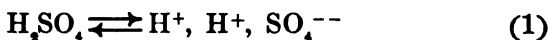


The positive sodium ion  $\text{Na}^+$  is attracted to the cathode, where it recovers its lacking electron, becomes an ordinary sodium atom, and decomposes water as follows:

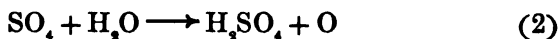


The chlorine ion  $\text{Cl}^-$ , with its excess electron, is attracted to the anode *A*, to which it gives up its excess, becomes ordinary chlorine, and either escapes as a gas or reacts with the constituents of the solution.

**Example 2. The electrolysis of sulfuric acid.** When sulfuric acid dissolved in water is electrolyzed, hydrogen is evolved at the cathode and oxygen at the anode (p. 14). From the standpoint of the theory of ionization these changes result in the following way: The sulfuric acid in dilute aqueous solution ionizes as follows:



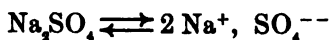
The hydrogen ions are attracted to the negatively charged cathode; upon recovering their electrons from the cathode, they unite to form hydrogen molecules ( $\text{H}_2$ ), and escape as hydrogen gas. The ions  $\text{SO}_4^{--}$  are attracted to the positively charged anode, give up their excess electrons, and immediately react with the water to form sulfuric acid and oxygen, as follows:



The oxygen atoms unite to form oxygen molecules ( $\text{O}_2$ ) and escape as oxygen gas. By comparing equations (1) and (2) it will be noted that the quantity of sulfuric acid represented as decomposed in equation (1) is the same as that regenerated in equation (2). The quantity, therefore, remains unchanged, and the process of electrolysis may be continued as long as any water is present. It will be noted that the hydrogen and oxygen evolved

come indirectly from the water, and are set free in the same ratio as that in which they are combined in it. The part played by the sulfuric acid in the electrolysis of water (p. 14) is thus made clear.

**Example 3. Electrolysis of sodium sulfate ( $\text{Na}_2\text{SO}_4$ ).** Sodium sulfate in aqueous solution ionizes as follows:



From what has been explained in the preceding examples one would expect such a solution, upon electrolysis, to yield sulfuric acid and oxygen at the anode and sodium hydroxide and hydrogen at the cathode. Experiment shows

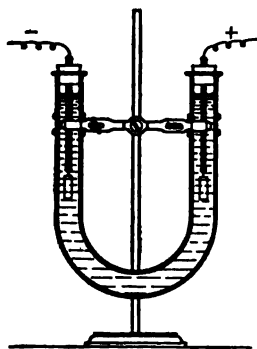


FIG. 79

that these results are actually obtained. Upon electrolysis the sulfates of other metals give similar results, forming sulfuric acid and oxygen at the anode, while at the cathode the metal is either deposited as such or reacts with the water present, depending upon its activity toward water

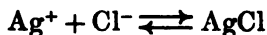
**Apparatus.** In the electrolysis of sodium sulfate the presence of the base  $\text{NaOH}$  about the cathode, and the acid  $\text{H}_2\text{SO}_4$  about the anode, may be demonstrated as follows: The electrolysis is effected in a U-tube (Fig. 79).

Before the circuit is closed, the solution in the arm of the tube which contains the cathode is colored with red litmus solution, while that in the other arm is colored with blue litmus. As the electrolysis proceeds, it will be found that the red litmus changes to blue, indicating the formation of a base, while the blue litmus changes to red, indicating the formation of an acid.

**Deductions from the theory of ionization.** If the theory, as outlined, presents a correct picture of the conditions existing in a solution of an electrolyte, certain logical deductions may be drawn at once:

1. Such a solution will have two independent sets of properties, *the one due to the molecules in solution, the other to the ions.*

All solutions containing a certain ion, say  $\text{Cl}^-$ , should have one set of properties, irrespective of the source of that ion. This is found to be true. For example, all chlorides which are electrolytes, when treated with a solution of silver nitrate ( $\text{AgNO}_3$ ), precipitate insoluble silver chloride ( $\text{AgCl}$ ). This may be regarded as due to an equilibrium which the silver and chlorine ions tend to set up with silver chloride:



But since the latter salt is practically insoluble, as soon as a very little of it is formed the solution becomes supersaturated and a precipitate results.

2. Since we assume that in very dilute solution the ionization is nearly complete, the color of the solution must be due to the several ions, rather than to the molecules; while in more concentrated solution the color due to the molecules will predominate. In accordance with this view we find that concentrated solutions of various salts of the same colored metal have quite a variety of colors, while their dilute solutions have the same color. Thus concentrated solutions of copper salts have various shades of blue, yellow, and green, while their dilute solutions, which give the copper ion  $\text{Cu}^{++}$ , are all pale blue and are not distinguishable in color.

3. In very dilute solutions in which the ionization is regarded as practically complete, the effect of the dissolved electrolyte upon the boiling and freezing points of the solvent, as well as upon the conductivity and osmotic pressure of the solution, should reach a maximum value. Thus the effect produced by sodium chloride ( $\text{NaCl}$ ) on complete ionization should be limited to twice that produced by an equivalent quantity of a non-electrolyte, such as sugar, while barium chloride ( $\text{BaCl}_2$ ), which forms three ions, should have a maximum effect of three times that of sugar. In a general way it may be said that such is the fact, though quantitative experiments do not always give the results which would be expected.

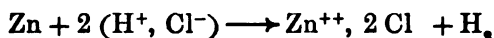
**II. The theory of ionization and acids.** In Chapter XIII we learned that acids constitute a class of compounds that (1) contain hydrogen, (2) taste more or less sour, (3) alter the color of indicators, and (4) neutralize bases forming salts. There are hundreds of acids, and it would certainly seem probable that so large a group of compounds having all these properties in common must have some common cause for this similarity in the make-up of their molecules. An inspection of the formulas of acids shows that the only constituent possessed by all acids is *hydrogen*. But many compounds that are not acids contain hydrogen, among these being sugars, starches, oils, and fats. So the presence of hydrogen in the molecule cannot be the whole explanation of acid properties.

Turning to our theory of ionization we first observe that *all acids are electrolytes*, and therefore form ions in solution. Further examination indicates that *the ionization of an acid always occurs in such a way as to produce hydrogen ions*. These are always positively charged (deficient in electrons) and are therefore cations. Substances that contain hydrogen, but give no hydrogen ions in solution, are not acids. In terms of our theory of ionization we may therefore define an acid as *a compound that in solution gives hydrogen ions*. A comparison of this definition with the more descriptive definition on page 205 will show that this is much more definite and is independent of all other substances, whereas the earlier definition depends largely upon the definition of a base.

**The action of acids upon metals.** We have seen that it is characteristic of the acids to act upon many of the metals in such a way as to yield hydrogen. Thus we prepared hydrogen according to the equation



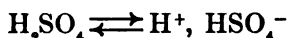
In terms of the ionization theory the equation should be written thus:



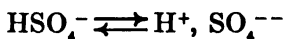
The  $\text{Cl}^-$  is the same on each side of the equation, so that the essential feature of the reaction is that the zinc passes into solution in the ion condition and an equivalent weight of hydrogen ceases to be ionic and becomes hydrogen gas. If we keep in mind that each plus sign (+) indicates the loss of an electron from the atom, we may describe the reaction by saying that the hydrogen atoms tend to hold all their electrons more firmly than do the zinc atoms. Consequently the hydrogen ion recovers its missing electron from the zinc, and the zinc atom in turn becomes an ion and passes into solution as such.

**Strength of acids.** Even a slight acquaintance with acids will convince one that they differ greatly in strength. Since the acid properties are attributed to the hydrogen ion, that acid should be the strongest which, *for a given weight of hydrogen in its solution*, produces the most hydrogen ions. This cannot be ascertained from the formula, for ionization is always an equilibrium, and the concentration of the hydrogen ions depends not only upon the weight of hydrogen in the acid of a given solution but also upon the percentage of the molecules which are ionized when equilibrium is reached. In the table on page 242 the strength of the common acids is expressed in percentage of ionization under definite conditions.

**The ionization of dibasic and tribasic acids.** In the case of dibasic acids such as sulfuric acid ( $\text{H}_2\text{SO}_4$ ), experiment shows that in *moderately concentrated* solutions the ionization is largely as follows:

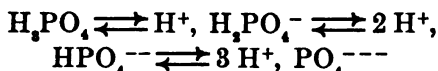


In *quite dilute solutions*, however, a second stage of ionization is reached:



In more concentrated solutions, therefore, sulfuric acid gives a much smaller *percentage* of its hydrogen in the form of ions than does a strong monobasic acid such as hydrochloric acid if the two are present in equivalent quantities, and the table shows that it is rated as much weaker. With the tribasic phosphoric

acid  $\text{H}_3\text{PO}_4$ , the ionization takes place in three successive stages, with increasing dilution, and may be represented as follows:

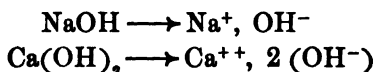


The ionization expressed in the final stage is very slight.

**Nonionizing solvents.** There are many solvents in which at least some of the acids are soluble, yet which do not occasion ionization of the acid. In the absence of all traces of water such solutions do not have the properties which we associate with the presence of acids. For example, dry  $\text{HCl}$  gas dissolved in benzene has no effect upon the color of indicators and is a nonelectrolyte.

**III. The theory of ionization and bases.** In Chapter XIV we have seen that bases constitute a class of compounds that (1) consist of a metal, together with both hydrogen and oxygen; (2) reverse the color changes in indicators produced by acids; and (3) destroy the characteristic properties of acids with the formation of water and a salt.

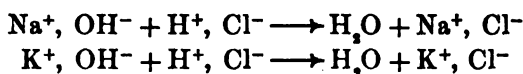
Examination of the solutions formed by all soluble bases shows that *all bases are electrolytes*; and consequently the bases, like the acids, form ions in solution. Further study shows that *they all yield the hydroxyl ion* ( $\text{OH}^-$ ). This ion carries a negative charge, which means that it carries one electron in excess of the number normally present in the two atoms that compose the ion. In terms of the theory of ionization *a base may be defined as a compound that in solution gives hydroxyl ions.*



**Strength of bases.** The ionization of a base, like that of an acid, is a reversible reaction leading to an equilibrium, and the percentage of ionization when equilibrium is reached varies greatly with different bases. As with acids, the largely ionized bases are the strong ones, while those which are little ionized

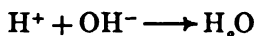
are weak. The table on page 242 gives the percentage of ionization of some of the commonest bases under stated conditions.

**The formation of water the essential fact of neutralization.** If now we turn to our theory of ionization, we see that it is the formation of water that is the fundamental fact in neutralization, and not the formation of a salt. The hydrogen ion of the acid ( $H^+$ ) and the hydroxyl ion of the base ( $OH^-$ ) unite quantitatively to form water, *which is practically an un-ionized compound*. The anion of the acid and the cation of the base are not affected by the reaction, but remain in solution as they were, namely, as equivalent ions of opposite charge. This is readily seen if we write an equation of neutralization in ionic form:



Hydrogen ions ( $H^+$ ) and hydroxyl ions ( $OH^-$ ) cannot coexist in the same solution, but will unite to form water until one or the other disappears. When both disappear, neutrality results.

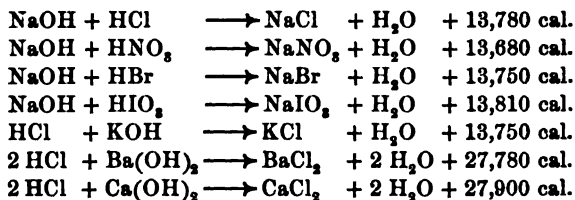
**Heat of neutralization.** The measurement of the heat of neutralization of various acids by various bases strongly supports the ionic view of neutralization. If the only reaction involved is the one represented by the equation



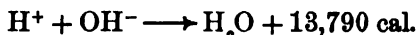
then the heat of neutralization should be the same in the case of all strongly ionized electrolytes. If the reaction is between two different *molecules*, as is represented in the equations on page 240, then every base should evolve a different quantity of heat with every different acid; for all the reactions will be different and it would be highly improbable that so many different reactions should chance to evolve the same heat.

The Danish chemist Julius Thomsen and the French chemist Berthelot were especially active in the measurement of the heat of reactions. Some of Thomsen's results are given in the table on the following page:

## HEAT OF NEUTRALIZATION: STRONG ELECTROLYTES

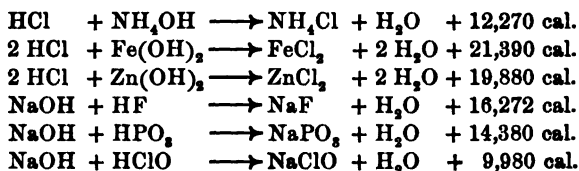


These figures indicate very clearly that the chemical action taking place in neutralization is practically *the same in all cases*, and we can write the equation thus:



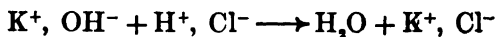
**Heat of neutralization of weak electrolytes.** In the case of weak acids or bases the ionization is only partial, even in dilute solutions. As neutralization proceeds more molecules are changed into ions. This change is a true chemical reaction and is attended by a heat change which may be either positive or negative. Accordingly, with weak acids or bases the heat of neutralization may be either greater or less than 13,790, and Thomsen found many examples of both kinds.

## HEAT OF NEUTRALIZATION: WEAK ELECTROLYTES

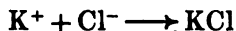


It will be seen that these figures also find a ready explanation by the theory of ionization.

**IV. The theory of ionization and normal salts.** From the discussion in the foregoing pages it will be seen that when neutralization is complete the cations of the base and the anions of the acid are left in equivalent quantities in the solution:



If the solution is very dilute, there will be very little union between these two species of ions. In a more concentrated solution a larger percentage of the ions will unite, resulting in the equilibrium

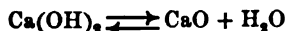


When the solution becomes saturated with the molecular member of the equilibrium (in this case KCl), either because of its limited solubility or through evaporation of the solvent, the excess separates in solid form as a salt.

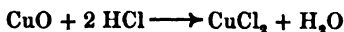
From the standpoint of the theory of ionization *a normal salt may be defined as a compound composed of the anion of any acid with the cation of any base.*

**General properties of normal salts.** Since there is no one ion characteristic of salts, there is no set of properties which they all have in common. In solubility they range between the widest limits, some dissolving to an extent of less than a milligram per liter, and others dissolving in much less than their own weight of water. In degree of ionization the salts are found to be much more nearly the same than is the case with either acids or bases. In a general way it may be said that *they are all strongly ionized* to about the same extent as strong acids and bases. The salts of magnesium, cadmium, zinc, and mercury are exceptional, being much less ionized than most other salts. The table on page 242 gives values for a few representative salts. The color of a salt is due in part to the acid and in part to the base from which the salt is derived. When both are colorless (as is true with the majority of both acids and bases), the salt is likely to be colorless. When either has a marked color, the salts are all apt to share it in some degree. Thus copper salts are usually some shade of blue or green, while the salts of the reddish chromic acid are usually yellow or orange.

**Preparation of salts from oxides.** Nearly all the metallic hydroxides, when heated, readily form the corresponding oxide. With calcium hydroxide the equation is as follows:



A number of oxides, among others that of calcium, are known to combine with water to form the hydroxide, so it seems probable that there is always an equilibrium between a metallic oxide, water, and the corresponding hydroxide. It is not surprising, therefore, that oxides suspended in water act upon acids just as do hydroxides to form salts. Thus copper oxide dissolves in hydrochloric acid to form copper chloride:



In a great many cases this is the most convenient way in which to prepare salts, since most of the oxides are more easily obtained than the corresponding hydroxides.

**Relative ionization of electrolytes.** Since *normal solutions* are all chemically equivalent to each other, it is convenient to indicate the degree of ionization of an electrolyte by stating the percentage ionized in its normal solution. The following tables will be found convenient for reference, though the values are merely approximate:

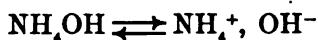
TABLE OF IONIZATION IN NORMAL SOLUTIONS

ACIDS	PER CENT	SALTS	PER CENT
Nitric . . . . .	85.0	Potassium chloride . . . . .	75.5
Hydrochloric . . . . .	79.0	Sodium chloride . . . . .	68.6
Sulfuric . . . . .	51.0	Ammonium chloride . . . . .	74.0
Acetic . . . . .	0.3	Potassium nitrate . . . . .	63.5
		Potassium acetate . . . . .	63.5
		Silver nitrate . . . . .	58.5
		Potassium sulfate . . . . .	54.7
		Potassium carbonate . . . . .	49.0
		Sodium sulfate . . . . .	46.0
		Zinc sulfate . . . . .	23.0
		Copper sulfate . . . . .	22.5
		Mercury salts . . . . .	Very little
BASES			
Potassium hydroxide . . . . .	76.0		
Sodium hydroxide . . . . .	72.0		
Barium hydroxide . . . . .	69.0		
Ammonium hydroxide . . . . .	0.3		
Calcium hydroxide (N/64) . . . . .	90.0		
(Very little soluble)			

TABLE OF IONIZATION AT OTHER CONCENTRATIONS

ACIDS IN N/10 SOLUTION	PER CENT	ACIDS IN CONCENTRATED SOLUTION	PER CENT
Acetic . . . . .	1.1	Hydrochloric (35%) . . . . .	13.6
Carbonic . . . . .	0.17	Nitric (62%) . . . . .	9.6
Hydrosulfuric . . . . .	0.07	Sulfuric (95%) . . . . .	0.7
Hydrocyanic . . . . .	0.01		

**Comment on the table.** A word of caution will be timely at this point. The student is likely to infer that a small degree of ionization, indicating a weak acid or base, means that a less quantity will be required in neutralization than when the acid or base is one that is strongly ionized. Thus the table shows that the solution of ammonium hydroxide is dissociated to the extent of only 0.3 per cent. It might be thought from this that when such a solution is treated with an acid, complete neutralization will occur when 0.3 per cent of the base has been acted on by the acid. This is not the case, as the indicator changes color only when *all* the base has been acted upon. In explanation, it must be remembered that the condition of ammonium hydroxide in solution is *an equilibrium*:

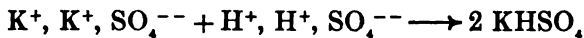


As fast as the hydroxyl ions ( $\text{OH}^-$ ) are removed by the reaction of neutralization, more are supplied by ionization of the base  $\text{NH}_4\text{OH}$ , so that all the base is finally brought into reaction.

**V. Theory of ionization and varieties of salts.** We have seen that the result of increasing the concentration of an electrolyte (say by evaporation) is to force the positive and the negative ions into union as molecules of a salt. If more than one kind of cations or anions (or both) are present in the solution, there will evidently be a number of possible combinations; and since it is the opposite electrical charges alone that cause two kinds of ions to unite, there will be no more reason for a given negative ion to unite with one kind of a positive ion rather than with any other save merely the relative number of the two that happen to be at hand. In addition to the normal salts whose formation we have already considered, we may often obtain *acid salts*, *basic salts*, and more rarely *mixed salts*.

1. **Acid salts.** If in a solution we have present some bivalent anion such as the ion  $\text{SO}_4^{--}$ , together with the hydrogen ion ( $\text{H}^+$ ) and some metallic cation such as  $\text{K}^+$ , there would seem to

be no good reason why these three should not unite to form the electrically neutral compound  $\text{KHSO}_4$ , and experiment shows that it is easy to get this compound. We can meet the necessary conditions by bringing together in solution potassium sulfate and sulfuric acid in equivalent proportions:



Since the product of the reaction is formed from the ions of an acid and a salt, and gives them again in solution, it is called an *acid salt*. From the ion standpoint *an acid salt may be defined as a salt composed of the ions of both an acid and a normal salt*.

2. **Basic salts.** If we prepare a solution that contains some bivalent cation such as the ion  $\text{Cu}^{++}$ , together with the hydroxyl ion ( $\text{OH}^-$ ) and some other univalent anion such as the ion  $\text{Cl}^-$ , it is evident that these three may unite to form the electrically neutral compound  $\text{Cu}(\text{OH})\text{Cl}$ . We may meet these conditions by bringing together copper chloride ( $\text{CuCl}_2$ ) and copper hydroxide ( $\text{Cu}(\text{OH})_2$ ):

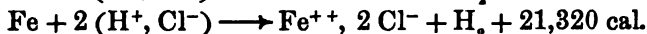
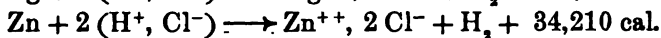
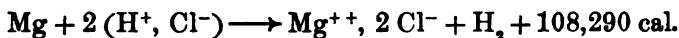


Since the product of this reaction is formed from the ions of a base and a salt, and gives them again in solution, it is called a *basic salt*. From the ion standpoint *a basic salt may be defined as a salt composed of the ions of both a base and a normal salt*.

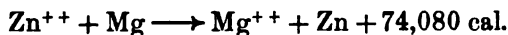
3. **Mixed salts.** We may also have salts of the type  $\text{KNaSO}_4$  or  $\text{Ca}(\text{NO}_3)\text{Cl}$ , in which one anion combines with two different metallic cations, or one cation with two different anions. Such salts are called *mixed salts*. The former type is far the more common, and we shall have occasional examples of such mixed types as we proceed.

VI. **The electrochemical series.** We have seen that when certain metals are brought into contact with an acid solution, hydrogen ions are discharged and an equivalent weight of the metal passes into solution in the ionic condition. The hydrogen ions recover their missing electron from the metallic atoms which are thus

seen to have a smaller affinity for their electrons than does hydrogen. This reaction is attended by considerable heat evolution, and experiment shows that the heat of reaction with various metals is quite different. For example, Thomsen found the following values for magnesium, zinc, and iron:



Now  $108,290 - 34,210 = 74,080$  cal. represents the difference in the energy liberated in the conversion of a gram-atomic weight of magnesium into ions in solution as compared with one of zinc. If, therefore, we bring magnesium into a solution containing zinc ions, we should expect the zinc to be displaced by the magnesium, with the liberation of 74,080 cal.



This is found to be the case. A very convenient experiment of the same kind can be made by sprinkling zinc dust into a solution of copper sulfate. The blue color of the solution soon disappears, and dark-brown copper powder is precipitated in place of the gray zinc. A thermometer in the solution will show a considerable rise in temperature at the same time. It is possible to arrange all the metals in the order in which they will displace each other in this way. Such an arrangement is known as the *electrochemical series of the metals* and is given in the following table:

#### ELECTROCHEMICAL SERIES OF THE METALS

1. Cæsium	8. Aluminium	15. Nickel	22. Antimony
2. Rubidium	9. Manganese	16. Tin	23. Mercury
3. Potassium	10. Zinc	17. Lead	24. Silver
4. Sodium	11. Chromium	18. <i>Hydrogen</i>	25. Palladium
5. Lithium	12. Cadmium	19. Copper	26. Platinum
6. Calcium	13. Iron	20. Arsenic	27. Gold
7. Magnesium	14. Cobalt	21. Bismuth	28. Osmium

All the metals above a given one in the series will displace it from solution, while it in turn will displace all those of lower position. The place of hydrogen in the series is most interesting. All those metals which precede it will, under ordinary conditions, evolve hydrogen from dilute acids, while those which follow will not.

The electrochemical series really represents the relative ease with which the various metallic atoms give up one or more electrons to form *positive* ions. Cæsium, the metal going into solution most readily, parts with an electron most easily, while such metals as gold and platinum retain their normal number of electrons most tenaciously. The nonmetallic elements can be arranged in a similar series, which represents the relative ease with which they *gain an excess* electron, and so become *negative* ions.

**Relative activities of the metals.** Having obtained a list of the metals that shows the order in which they tend to pass into ionic form, it is natural to inquire whether the same list indicates the relative activities of the metals in other types of reactions. For example, nearly all the metals combine directly with oxygen, and it is not difficult to measure the heat of such reactions.

Experiment has shown that if we tabulate the metals in the order of their heats of combustion, we get the very same list that we have obtained for relative ease of ion formation. Because of this fact this list is often called the *activity series* rather than the *electrochemical series*.

**VII. Indicators.** From time to time in the preceding pages mention has been made of indicators as a means for determining the point of neutrality. A great many compounds may be used for this purpose, some of which occur in nature. Indeed, the water extract of many colored flowers such as violets or corn-flowers or of colored leaves such as red cabbage, or the juices of fruits such as blackberries, will serve the purpose. The ones most frequently used in the laboratory are as follows:

TABLE OF INDICATORS

NAME OF INDICATOR	ACID SOLUTION	BASIC SOLUTION
Litmus . . . . .	Red	Blue
Phenolphthalein . . . . .	Colorless	Purplish-red
Methyl orange . . . . .	Red	Yellow
Congo red . . . . .	Blue	Red
Cochineal . . . . .	Yellowish-red	Purple

These indicators do not all change color at the same point. Some require a very slight excess of the hydroxyl ion to produce the color change, and some require an excess of hydrogen ions. Litmus changes color most nearly at the exact point of neutrality. By very careful measurement it is possible to determine the concentration of hydrogen ions or hydroxyl ions required to change the color of a given indicator. The indicator can then be used not to determine the point of neutrality but to indicate the exact excess of acid or base present, especially in cases in which the excess is so small as to be difficult to determine by an ordinary laboratory measurement.

### QUESTIONS

1. In the electrolysis of sodium sulfate why do we expect sodium hydroxide to be formed at the cathode and sulfuric acid at the anode?
2. What would be the objection (aside from cost) to making sulfuric acid in this way?
3. Trace the details of the electrolysis of calcium chloride,  $\text{CaCl}_2$ .
4. (a) Why should nearly all the soluble salts of manganese have the same (pink) color in solution? (b) Potassium permanganate ( $\text{KMnO}_4$ ) forms a solution of a deep purple color. What inference would you draw as to the state of the manganese in this compound?
5. So far as you can judge, which should be the best conductor of the electrical current—a normal solution of sulfuric acid, of sodium hydroxide, or of potassium chloride?
6. What place in the electrochemical series does copper occupy in reference to hydrogen? How would you expect a solution of copper sulfate to act when electrolyzed?

7. In precipitating zinc from a solution of zinc salts by magnesium will the use of different salts of zinc make any difference in the amount of heat evolved?

8. Why should there be little reunion between the positive ions and the negative ions in a dilute solution?

#### PROBLEMS

1. How much copper will be thrown out of a solution of copper sulfate by the addition of 60 g. of zinc?

2. If aluminium and zinc cost the same per pound, what would be the relative cost in precipitating copper from copper sulfate by the use of these two metals?

3. How much heat will be evolved when 100 g. of sodium hydroxide in solution is neutralized with dilute sulfuric acid?

4. A normal solution of an acid was exactly neutralized by a normal solution of a base, and 1000 cal. of heat was evolved. What was the volume of each solution used?

## CHAPTER XVII

### COMPOUNDS OF NITROGEN

**Occurrence.** Although large quantities of nitrogen occur in the atmosphere, it is all in the free state, with the exception of a comparatively small amount, which is present in the form of ammonia and oxides of nitrogen. In the earth's crust, on the other hand, there occur in certain localities considerable deposits of compounds of nitrogen, especially of sodium nitrate ( $\text{NaNO}_3$ ) and potassium nitrate ( $\text{KNO}_3$ ). Moreover, such compounds are present in small quantities in all productive soils. From these soils the nitrogen is taken up by plants and built into complex compounds. Animals feeding on these plants assimilate the nitrogenous matter, which becomes an essential part of the animal tissue. In both plants and animals the nitrogen is present chiefly in the form of protein matter, which consists of complex compounds containing the elements carbon, nitrogen, oxygen, and hydrogen, and sometimes phosphorus and sulfur.

**The unstable character of compounds of nitrogen.** Experiment shows that the molecule of nitrogen has the formula  $\text{N}_2$ , and that the element is very inactive at ordinary temperatures. This inactivity is due to the fact that the nitrogen molecule is very stable so that a great deal of energy is required to separate it into its atoms, into which form it must be converted before entering into combination with other elements. On the other hand, when nitrogen occurs as a constituent of a compound, the nitrogen atoms tend to leave the compound and form stable nitrogen molecules. As a result of this tendency compounds containing nitrogen are apt to be unstable. It is partly due to the unstable character of certain nitrogenous compounds that they are so extensively used as a constituent of explosives.

While a great many compounds of nitrogen are known, it is desirable at this time to discuss only some of the more simple ones, namely, those which nitrogen forms with hydrogen and oxygen.

#### COMPOUNDS OF NITROGEN WITH HYDROGEN

Nitrogen forms three important compounds with hydrogen, the names and formulas of which are as follows: ammonia ( $\text{NH}_3$ ), a colorless, gaseous compound of characteristic odor; hydrazine ( $\text{N}_2\text{H}_4$ ), a colorless liquid boiling at  $118^\circ$ ; hydronitric acid ( $\text{HN}_3$ ), a very unstable, colorless liquid boiling at  $37^\circ$ .

**Ammonia.** Inasmuch as ammonia is formed in certain natural processes which are constantly taking place about us, such as the decay of nitrogenous organic matter, it is easy to understand why this compound has been known for so long a time. It was originally prepared by heating such tissues as the hoofs and horns of animals, and the aqueous solution of the gas so obtained was termed *spirits of hartshorn*. The pure gas itself was first prepared by Priestley, in 1774, and its composition was determined soon after by the French chemist Berthollet.

**Preparation of ammonia.** Ammonia can be prepared in a number of ways, the most important of which are the following:

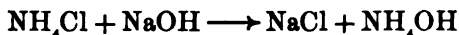
1. **Synthetic method.** When a mixture of hydrogen and nitrogen is heated or when it is subjected to the action of an electric discharge, a small percentage of ammonia is formed. The small yield is due to the fact that an equilibrium results as expressed in the following equation:



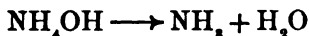
The best yields, so far, have been obtained by a method devised by the German chemist Haber and known as the *Haber process*. This method consists in heating a mixture of nitrogen and hydrogen under a pressure of 200 atmospheres to a temperature of about  $500^\circ$ , in contact with a suitable catalyzer such as finely divided iron. Under these conditions about 8 per cent of the nitrogen combines with hydrogen. The gases are then passed

through water which dissolves the ammonia, while the uncombined hydrogen and nitrogen pass on and are again heated. The process thus becomes continuous, additional hydrogen and nitrogen being introduced as required. This method was used by the Germans on a large scale in the World War. Extensive experiments are being conducted in the United States to perfect the process so that it may be used commercially in this country.

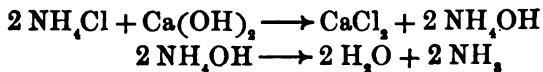
2. *Laboratory method.* In the laboratory, ammonia is usually prepared from ammonium chloride ( $\text{NH}_4\text{Cl}$ ), a white solid obtained in the manufacture of coal gas. When a mixture of ammonium chloride and sodium hydroxide is heated in the presence of a small quantity of water, the ammonium radical (p. 152) and sodium change places, as expressed in the following equation:



The resulting ammonium hydroxide ( $\text{NH}_4\text{OH}$ ) is unstable and, as fast as it is formed, breaks down into water and ammonia:



Calcium hydroxide ( $\text{Ca}(\text{OH})_2$ ) is frequently used in place of the more expensive sodium hydroxide:



**Experimental details.** The preparation is conducted as follows: The mixture of ammonium chloride and calcium hydroxide is introduced into a flask with a little water (Fig. 80, A) and gently heated. Ammonia is evolved and may be collected by bringing the end of the exit tube inside

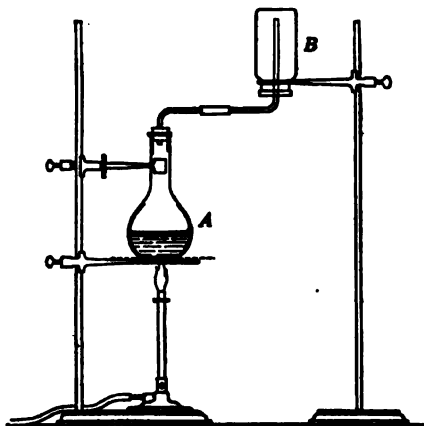


FIG. 80

and near the bottom of an inverted bottle *B*, as shown in the figure. The gas, being lighter than air, collects in the bottle, gradually forcing the air out at the mouth. Because of its great solubility it is not practicable to collect ammonia over water, as in the case of oxygen and hydrogen. In place of water, however, one may use some liquid, such as mercury, in which the ammonia is not soluble. As ordinarily prepared in the laboratory, it is collected by simply displacing the air in a bottle, as described above.

In addition to this method, ammonia is often obtained in the laboratory by heating an aqueous solution of the gas. Such a

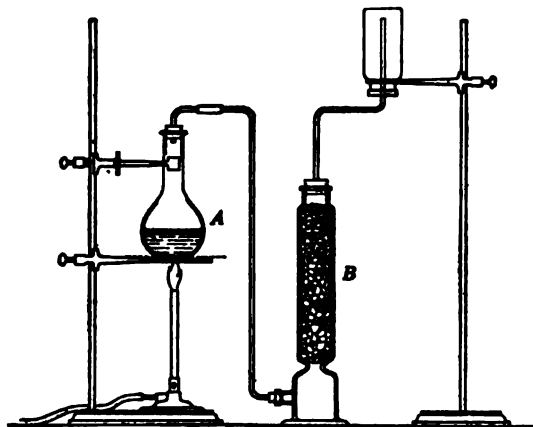


FIG. 81

solution is a common article of commerce, and is sold under the name *ammonia water*, or *aqua ammonia*. The solution is placed in a flask *A* (Fig. 81) and a gentle heat applied. Ammonia is evolved and is passed through a cylinder *B* filled with small pieces

of lime, which serve to absorb the water vapor. The pure gas so obtained may be collected by the displacement of air, as described above.

**Commercial preparation.** At present ammonia is obtained commercially in the process of manufacturing coal gas and coke. Certain grades of bituminous, or soft, coal are best adapted for this purpose. Such coal contains, in addition to carbon, about 1 per cent of nitrogen and 7 per cent of hydrogen, as well as small percentages of other elements. When such coal is heated in retorts from which the air is excluded, complicated changes take place, resulting not only in the formation of the combustible gases which constitute coal gas but also of ammonia and many other valuable products. From 25 to 50 per cent of the nitrogen present in the coal is converted into ammonia. The volatile matter expelled from the

coal is passed through water, which absorbs the ammonia together with certain other compounds, forming a solution known as the *ammoniacal liquor*. When this liquor is heated with slaked lime, ammonia is evolved and may be passed into pure cold water, forming ordinary aqua ammonia.

**Properties.** Ammonia is a colorless gas having a strong, suffocating odor. Under standard conditions 1 l. of the pure gas weighs 0.7708 g., being 0.59 times as heavy as air. Its critical temperature is  $131^{\circ}$ , at which temperature it is liquefied by a pressure of 113 atmospheres. Liquid ammonia is colorless and boils at  $-33.5^{\circ}$ . The properties of liquid ammonia have been extensively studied by E. C. Franklin, who has shown that, like water, it is not only an excellent solvent but also a highly ionizing one. At still lower temperatures ammonia can be obtained in the form of a snowlike solid melting at  $-75.5^{\circ}$ .

A noteworthy property of ammonia is its extreme solubility in water. Under a pressure of 1 atmosphere, 1 l. of water dissolves 1298.9 l. of the gas at  $0^{\circ}$ , and 710 l. at  $20^{\circ}$ . On account of the expansion of the liquid the resulting solutions have a density less than that of water, as is shown in the following table:

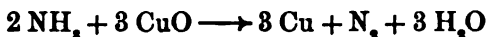
Density . . .	1.00	0.995	0.990	0.980	0.970	0.950	0.930	0.910	0.890	0.880
Percent by weight of $\text{NH}_3$ . . .	0.00	1.14	2.31	4.80	7.31	12.74	18.64	24.99	31.73	35.60

**Chemical conduct.** The chemical properties of ammonia may be conveniently discussed under the following heads:

1. *Dissociation of ammonia.* At ordinary temperatures ammonia is a stable compound. When heated to a high temperature, however, or when subjected to the action of electric sparks, it is dissociated into its elements. The reaction is a reversible one. Thus, when electric sparks are passed through ammonia, equilibrium results when about 96 per cent of the compound is dissociated (p. 250).

2. *Reducing action of ammonia.* When heated, ammonia acts as a strong reducing agent, owing to the hydrogen which is liberated from the compound under the influence of heat. This

reducing property may be shown by passing the gas through a tube containing a metallic oxide, such as oxide of copper, heated to a high temperature. The oxide is reduced to the metal:



8. *Relation to combustion.* Because of the hydrogen present in ammonia, and because of the comparative instability of the compound, the gas readily burns in an atmosphere of pure oxygen.

The combustion will not take place in air, however, unless heat is continuously applied from an external source.

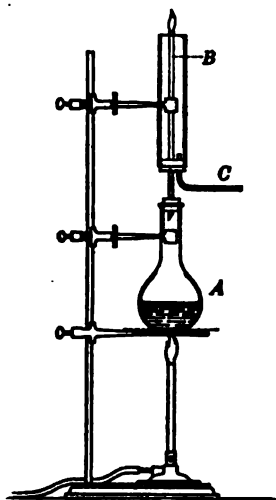
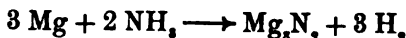


FIG. 82

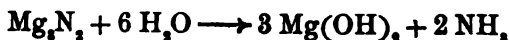
**Combustion of ammonia.** The combustion of ammonia may be shown in the following way: Some aqua ammonia is poured into the flask *A* (Fig. 82) and heated gently. Ammonia escapes and may be ignited by holding a Bunsen flame at the end of the exit tube *B*. Combustion ceases, however, as soon as the flame is withdrawn. If, now, oxygen is passed in through the tube *C*, the ammonia escaping from *B* is surrounded by pure oxygen and, if ignited, will continue to burn.

4. *Reaction with oxygen.* When a mixture of ammonia and air is heated in contact with platinum as a catalyzer, the ammonia is oxidized by the oxygen of the air to nitric acid. During the World War this reaction was utilized by the Germans for the preparation of nitric acid (p. 262).

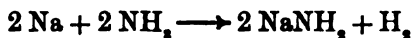
5. *Action upon metals.* A number of the metals, such as magnesium and lithium, react with ammonia at high temperatures, displacing all the hydrogen and forming nitrides:



These nitrides are solids and react with water to form ammonia:



On the other hand, the metals sodium and potassium act upon ammonia to replace only a part of the hydrogen :



The radical  $\text{NH}_2$  is termed the *amido*, or *amino*, group, so that the compound  $\text{NaNH}_2$  is termed *sodamide*. It is a white solid and, like the nitrides, reacts with water to form ammonia. Its chief use is in the preparation of sodium cyanide and indigo.

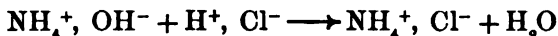
6. *Action upon salts.* Ammonia combines directly with a number of salts to form complex compounds. In some of these compounds, such as that represented by the formula  $\text{CaCl}_2 \cdot 8 \text{ NH}_3$ , the ammonia seems to play much the same part as does the water in hydrates.

7. *Action toward water.* It will be recalled that ammonia is extremely soluble in water, and that the resulting solution (aqua ammonia) is basic in character (p. 175). These properties are accounted for by the fact that ammonia and water enter into chemical combination with each other and that the resulting compound, ammonium hydroxide ( $\text{NH}_4\text{OH}$ ), ionizes to form the two univalent ions  $\text{NH}_4^+$  and  $\text{OH}^-$ , the latter imparting to the solution its basic character. In this solution the ammonium hydroxide is in equilibrium not only with ammonia and water but also with the ions  $\text{NH}_4^+$  and  $\text{OH}^-$ , as expressed in the following equation :



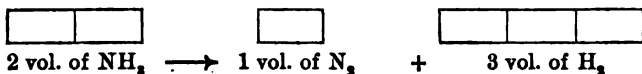
When heated, aqua ammonia acts as if it were solely a solution of ammonia in water, for as fast as the ammonia is driven out by the heat, the equilibrium existing among the different substances represented in the equation is disturbed, with the result that more ammonia is formed. If the heating is continued, therefore, all the ammonia is finally driven out. On the other hand, when acted upon by an acid, aqua ammonia acts as if it were solely a solution of ammonium hydroxide, for as fast as the ammonium hydroxide present is neutralized by the acid,

more is formed as long as any free ammonia remains in solution. Thus, when hydrochloric acid is added to aqua ammonia, ammonium chloride and water are formed:



On evaporating the water, the ammonium chloride is left in the form of a white solid. Similarly, nitric and sulfuric acids form respectively ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ) and ammonium sulfate ( $(\text{NH}_4)_2\text{SO}_4$ ).

**Composition of ammonia.** That ammonia is a compound of nitrogen and hydrogen is proved by the fact that it may be formed by the direct union of the two elements. The quantitative composition of the compound may be determined by taking advantage of certain reactions which make it possible to liberate the nitrogen as well as the hydrogen from any definite volume of ammonia. By measuring the volumes of the gases so liberated one can compare them not only with each other but also with the volume of the ammonia from which they were derived. In this way it has been proved that on decomposition 2 volumes of ammonia yield 1 volume of nitrogen and 3 volumes of hydrogen, as expressed graphically in the following equation:



Of course, the reverse is likewise true: 3 volumes of hydrogen combine with 1 volume of nitrogen to form 2 volumes of ammonia (compare with the composition of water, p. 84). By comparing the weight of the 3 volumes of hydrogen with that of the 1 volume of nitrogen we can determine the proportion by weight in which these two elements combine to form ammonia. The results are expressed by the formula  $\text{NH}_3$ , which indicates that 14.01 parts by weight of nitrogen combine with 3.024 of hydrogen to form 17.034 parts of ammonia.

**Uses of ammonia.** Large quantities of ammonia are used in the manufacture of aqua ammonia, as well as in the formation

of ammonium compounds, such as ammonium chloride and ammonium sulfate. In the liquid state it is also used extensively in the manufacture of artificial ice. Its use for this purpose is based on the facts that the gas is easily liquefied by pressure and that the resulting liquid has a relatively high heat of vaporization.

**The manufacture of ice.** The general method used in the manufacture of ice may be understood by reference to Fig. 83. Ammonia is liquefied by means of a compressor pump and led into the pipes *A*, *B*. The heat of condensation is absorbed by water flowing over the pipes. These pipes lead into coils in a large tank nearly filled with brine, prepared by dissolving calcium chloride in water. By means of an expansion valve *C* the pressure upon the liquid ammonia is diminished as it enters the coils, and the heat absorbed by the rapid evaporation of the liquid lowers the temperature of the brine below  $0^{\circ}$ . Metal vessels *D*, *E*, *F* filled with pure water are lowered into the cold brine and left until the water in them is frozen into cakes of ice. The gaseous ammonia resulting from the vaporization is led through *G* back to the compressor pump, by which it is again liquefied, so that the process is continuous.

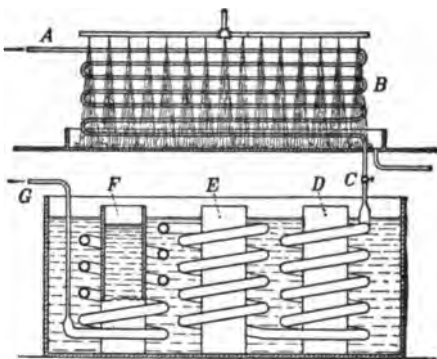


FIG. 83

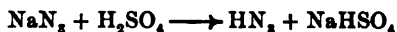
**Hydrazine ( $N_2H_4$ ).** This compound may be regarded as ammonia in which an atom of hydrogen has been displaced by the univalent radical  $NH_2$ . Its formula may therefore be written  $NH_2-NH_2$ . It is formed by the reduction of hyponitrous acid ( $H_2N_2O_2$ ), but is most readily obtained by complicated reactions with certain organic compounds. When an aqueous solution is distilled, the hydrate ( $N_2H_4 \cdot H_2O$ ) is obtained. The free hydrazine is prepared from this hydrate by distilling it under diminished pressure with some compound, such as barium oxide, that has a strong affinity for water.

Hydrazine is a colorless liquid boiling at  $113.5^{\circ}$ . Like ammonia, it combines with water to form a base from which salts can be prepared by the action of acids. For example, with hydrochloric acid it forms hydrazine hydrochloride, a white solid having the formula  $N_2H_4 \cdot HCl$ .

**Hydronitric acid ( $\text{HN}_3$ ).** This acid, known also as hydrazoic acid, was first obtained by Curtius in 1890, and the properties of the acid, as well as its salts, have been extensively studied by Dennis and his associates. Its sodium salt may be prepared by the action of nitrous oxide (a gas having the formula  $\text{N}_2\text{O}$ ) on sodamide:



An aqueous solution of the free acid may be obtained from the sodium salt by adding dilute sulfuric acid and distilling:



The pure acid is a colorless liquid of disagreeable odor. It boils at  $37^\circ$  and is violently explosive, dissociating into its constituent elements with the liberation of considerable heat. It has the general properties of a weak acid, dissolving certain metals, such as zinc and iron, forming the corresponding salts and evolving hydrogen. The salts of hydronitric acid are solids, most of them being colorless. Some of them are violently explosive and all, on being heated, decompose, evolving nitrogen and leaving the metal uncombined.

**Representation of valence.** It is often desirable to represent in some graphic way the valence of an element present in a compound, and various convenient methods have been employed. The usual method is to draw lines between the symbols, each line representing a unit of valence. Thus the formula for hydrochloric acid is sometimes written  $\text{H}-\text{Cl}$ , the line indicating that both hydrogen and chlorine are univalent in this compound. Likewise, the formula for water may be written  $\text{H}-\text{O}-\text{H}$  or  $\text{O} < \overset{\text{H}}{\underset{\text{H}}{\text{H}}}$ , indicating that oxygen is bivalent and hydrogen univalent.

Similarly, the formulas  $\text{N} < \overset{\text{H}}{\underset{\text{H}}{\text{H}}}$  and  $\text{Cl} > \text{N} < \overset{\text{H}}{\underset{\text{H}}{\text{H}}}$  represent ammonia and ammonium chloride, the nitrogen in the former compound being trivalent and in the latter pentavalent.

This method of indicating valence is very convenient, but it may lead to inaccurate language and erroneous ideas. Thus we sometimes say that two elements are joined or united by two valences, as in the case of calcium oxide. This is a brief but not very accurate way of stating the fact that both calcium and oxygen are known to be bivalent, and that the oxide is represented by the formula  $\text{Ca}=\text{O}$ . It is not valence which unites these elements, but chemical affinity.

The use of lines to represent valence is also open to the objection of conveying the impression that the various atoms are rigidly united in some way, and this impression is strengthened by the fact that these lines are usually called *bonds* or *links*. There is no evidence for any such rigid union, nor can we well imagine how there can be any. On the other hand, we know that the atoms in a molecule maintain an orderly relation to each other, and these valence lines merely serve to indicate this relation.

**Structural formulas.** Formulas with lines indicating the valence of each element are called *structural*, or *graphic*, formulas. In these formulas an attempt is made to represent in a general way the actual relations of the atoms in the molecule. Thus the structural formula of water,  $\text{H}-\text{O}-\text{H}$ , tells us that in the molecule of water the hydrogen atoms are joined to the oxygen atom and not to each other. Likewise the structural formula for ammonia expresses our belief that each of the hydrogen atoms in a molecule of the compound is joined to the nitrogen.

The determination of the arrangement or relative grouping of the atoms within the molecule of any compound is based upon a study of the general properties and chemical conduct of the compound. The problem is not a simple one, and its solution often depends upon many assumptions, so that the structural formulas of many compounds are unknown, while in other cases the formulas assigned are very uncertain.

## COMPOUNDS OF NITROGEN WITH HYDROGEN AND OXYGEN

The most important of these compounds are the following:

Hyponitrous acid ( $\text{H}_2\text{N}_2\text{O}_2$ ), a colorless, unstable solid.

Nitrous acid ( $\text{HNO}_2$ ), known only in dilute solution.

Nitric acid ( $\text{HNO}_3$ ), a colorless liquid.

Hydroxylamine ( $\text{NH}_2\text{OH}$ ), a white, crystalline solid.

The solutions of the first three of these compounds are acids, as is indicated by the names; the solution of the last is a base. Nitric acid will be described first, since it is by far the most important compound of the group.

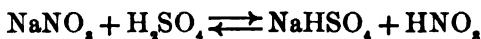
**Nitric acid.** Nitric acid was well known to the alchemists, being first prepared by the Egyptians. In the ninth century the alchemist Geber prepared it from saltpeter ( $\text{KNO}_3$ ) by a process

somewhat similar to that used at the present time, and the Germans still call it *Salpetersäure*. The composition of the acid was first determined by Lavoisier and Priestley.

Because of its great activity, nitric acid does not occur free in nature, but a number of its salts are found in considerable quantities. The most abundant of these is sodium nitrate, which is found chiefly in Chile, and hence is known as Chile saltpeter.

**Preparation of nitric acid.** Nitric acid can be prepared by a number of different methods, the most important of which are the following:

1. *Preparation from sodium nitrate.* Nitric acid is prepared, both in the laboratory and commercially, by the action of sulfuric acid upon sodium nitrate. When brought together, sulfuric acid and sodium nitrate react to form sodium hydrogen sulfate and nitric acid, as expressed in the following equation:



The reaction is a reversible one, and at ordinary temperatures equilibrium soon results. If, however, a gentle heat is applied to the mixture, the nitric acid is removed as fast as formed,

since it has a relatively low boiling point ( $86^\circ$ ), and may be recovered by condensing the vapors. Under these conditions the reverse reaction cannot take place, and the action between the sodium nitrate and the sulfuric acid continues until it is completed.

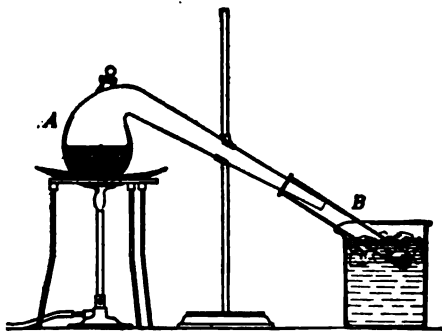
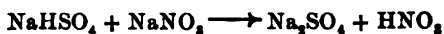


FIG. 84

If double the weight of sodium nitrate indicated in the equation is used, and the mixture is heated to a higher temperature, the sodium hydrogen sulfate which is first formed reacts with the excess of sodium nitrate to form the normal sodium sulfate and nitric acid:



This additional amount of nitric acid is formed without using any additional sulfuric acid. The higher temperature required to bring about the reaction, however, partly decomposes the nitric acid so that the process is not an economical one.

The preparation of nitric acid in the laboratory may be conducted as follows: sodium nitrate is introduced into a retort *A* (Fig. 84) and sulfuric acid added. If the retort is gently heated, the nitric acid distills over as fast as formed, and is condensed in a tube *B* kept cool by ice water.

**Commercial preparation of nitric acid.** Fig. 85 illustrates a form of apparatus used in the preparation of nitric acid on a large scale. Sodium nitrate and sulfuric acid are heated in the iron retort *A*. The resulting acid vapors pass in the direction indicated by the arrows, and are condensed in the tubes *B*, kept cool by streams of water. These tubes are inclined so that the liquid resulting from the condensation of the vapors runs back into *C* and is drawn off into the large vessel *D*.

Because of the unstable character of nitric acid a certain amount of decomposition always takes place when it is

distilled under ordinary atmospheric pressure. To prevent this the process is often carried out under diminished pressure and in a current of oxygen.

**2. Preparation from air.** When electric sparks are passed through air, a portion of the nitrogen and oxygen present combine to form a colorless gaseous compound known as nitric oxide, which has the formula  $\text{NO}$ . As fast as it is formed, this oxide combines with more oxygen to form nitrogen dioxide ( $\text{NO}_2$ ), a reddish-brown gas. When the dioxide is brought in contact with water, the two react to form nitric acid. The equations for the reactions are as follows:

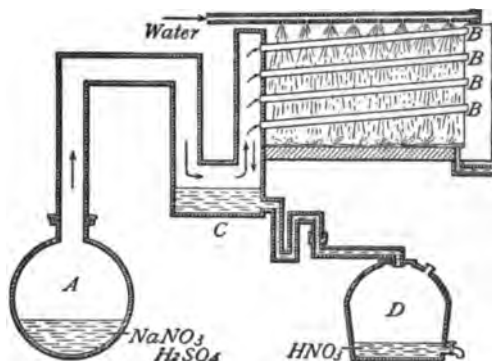
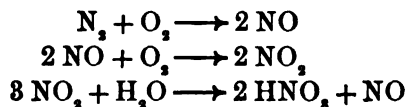


FIG. 85

From the acid so obtained, its various salts (the nitrates) may be prepared by neutralization with the appropriate bases. Inasmuch as large quantities of the nitrates are in demand in the manufacture of fertilizers, and since the supply of these compounds in nature is limited, repeated efforts have been made to prepare both nitric acid and the nitrates from the inexhaustible supplies of oxygen and nitrogen in the atmosphere, utilizing the above reactions. The method has not as yet proved a marked success, on account of the cost of generating the electric current. It has been greatly improved, however, by Birkeland and Eyde, and their process is in use in Norway, where the waterfalls are utilized for the generation of electrical energy.

**Birkeland and Eyde process.** In the Birkeland and Eyde process an electric arc is produced by forcing a powerful alternating current between two copper electrodes so placed that the arc passes between the poles of an electro-

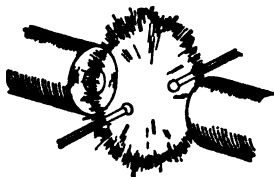


FIG. 86

magnet (Fig. 86). By the action of the magnet the arc is spread out into disks about 2 m. in diameter. The apparatus is inclosed in a large tube in such a way that air forced through the tube is subjected to the action of the electric discharge. The greater efficiency of this process lies in the fact that, by the spreading out of the arc into disks, larger quantities of air come under its influence. The nitrogen dioxide so

formed is passed into water, and a dilute solution of nitric acid is obtained. The cost attending the concentration of the acid is so great that it has not been found economical to prepare the pure acid by this method, but the dilute solution is being used to some extent in the preparation of nitrates.

**3. Preparation from ammonia.** Nitric acid is easily prepared by heating a mixture of ammonia and air in contact with platinum, which acts as a catalytic agent. This method, although at present more expensive than the sodium nitrate method for the commercial manufacture of the acid, will probably come into general use, for the supply of sodium nitrate is limited and will not last many years.

During the World War the Germans were unable to secure the necessary supplies of sodium nitrate for the preparation of nitric acid and so

used the ammonia method. The raw materials required in this method are (1) nitrogen and (2) hydrogen used in the preparation of the ammonia, and (3) oxygen (air) used in oxidizing the ammonia to nitric acid. Of these materials, nitrogen and oxygen are obtained directly from the air, while the hydrogen is prepared by the action of steam upon carbon under proper conditions (see water gas).

It is safe to say that the Germans would never have declared war had they not first perfected a method for obtaining the nitric acid necessary for the manufacture of explosives from sources other than sodium nitrate; for they must have recognized the strong probability that in case of war they would not be able to secure the necessary supplies of sodium nitrate, all of which had to be shipped from Chile.

**Preparation of pure nitric acid (hydrogen nitrate).** Pure nitric acid (more properly called hydrogen nitrate, to distinguish it from its aqueous solutions) readily decomposes into water, nitrogen dioxide, and oxygen, as represented in the following equation:



The nitrogen dioxide resulting from the decomposition is a reddish-brown gas which dissolves in the liquid, giving it a yellowish color. Because of its unstable character, hydrogen nitrate is difficult to prepare. By heating sulfuric acid and sodium nitrate in a retort under diminished pressure and cooling the resulting filtrate, the pure hydrogen nitrate is obtained in the form of a snowlike solid melting at  $-41.3^\circ$ . As this melts, a slight decomposition takes place, but the resulting liquid is called pure nitric acid.

**Properties.** Nitric acid is a colorless liquid. It has a density of 1.51, and boils at  $86^\circ$  with partial decomposition. An aqueous solution containing 68 per cent of the acid has a constant boiling point (p. 179) and distills with unchanged concentration. This solution has a density of 1.4 and constitutes the concentrated acid of commerce.

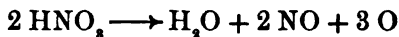
**Chemical conduct of nitric acid.** Some of the most important reactions of nitric acid are the following:

1. **Acid properties.** As the name indicates, it is an acid and has all the properties characteristic of that class of substances.

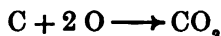
When dissolved in water it forms the ions  $\text{H}^+$  and  $\text{NO}_3^-$ . The solution changes blue litmus red and neutralizes bases forming salts. It is one of the strongest of acids (p. 237).

2. *Unstable character.* The unstable character of nitric acid has already been described in a preceding paragraph.

3. *Oxidizing action.* Since nitric acid contains a large percentage of oxygen and readily decomposes with evolution of oxygen, it serves as a strong oxidizing agent. Under ordinary circumstances, in the presence of a substance readily oxidized, the acid decomposes according to the following equation:



In such cases oxygen is not evolved, but enters into combination with the oxidizable substance present. In this way carbon, when heated with nitric acid, is oxidized to carbon dioxide:

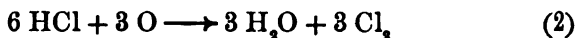


4. *Action upon organic compounds.* Nitric acid readily reacts with many organic substances, forming compounds of great importance. Thus, with ordinary glycerin it forms the compound known as *nitroglycerin*, which is the explosive constituent of dynamite; likewise, with cellulose, the principal constituent of wood-fiber, it forms various *nitrocelluloses*, which are used in making smokeless gunpowder. When nitric acid acts upon protein matter, a yellow compound known as xanthoprotein is formed; hence nitric acid in contact with the skin produces a yellow stain.

5. *Action with hydrochloric acid; aqua regia.* When nitric acid acts as an oxidizing agent, it usually decomposes, as represented in the following equation:



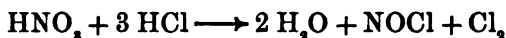
If hydrochloric acid is present, the oxygen, as fast as formed, reacts with the acid according to the following equation:



The nitric oxide formed according to equation (1) is not evolved as such, but combines with the chlorine liberated according to equation (2) to form an orange-yellow, gaseous compound known as nitrosyl chloride (NOCl):



These three equations may be combined into the single equation :



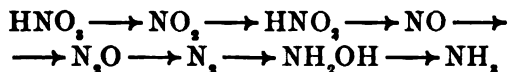
When concentrated nitric and hydrochloric acids are mixed, the reaction expressed in the above equation takes place slowly. In the presence of some substance, such as a metal, which will unite with the chlorine as fast as it is formed, the speed of the reaction is greatly increased. This mixture of nitric and hydrochloric acids is termed *aqua regia*, and is prepared by adding 1 volume of nitric acid to 3 volumes of hydrochloric acid. It acts upon metals and other substances more energetically than either of the acids separately, and owes its solvent power not to its acid properties but to the action of the chlorine which is liberated. Consequently, when it acts upon metals it converts them into chlorides.

It may be added that this mixture was well known to the alchemists, who termed it *aqua regia* because of its strong solvent powers. It is evident that any other mixture of substances, the constituents of which interact to liberate chlorine, has a similar solvent power.

6. *Action upon metals.* All the metals, with the exception of gold, platinum, and a few of the rare metals, are acted upon more or less readily by nitric acid. In discussing the action of nitric acid upon these metals it is convenient to divide them into two classes:

(a) *Metals occurring above hydrogen in the electrochemical series.* It will be recalled that any of the metals occurring above hydrogen in the electrochemical series of the metals (p. 245) will in general liberate hydrogen from dilute acids. At first

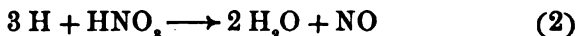
thought it might be expected that nitric acid would act upon these metals in a similar way. When one recalls, however, that nitric acid is a strong *oxidizing* agent, while hydrogen has strong *reducing* properties, it seems reasonable to suppose that nitric acid would be reduced by the hydrogen, yielding reduction products. Experiments show that this is what actually happens. The particular reduction products formed in any case depend upon the metal, the concentration of the acid, the temperature, and other conditions under which the reaction takes place. The following compounds represent successive steps in the reduction of nitric acid:



It is possible, by selecting different metals and by modifying the conditions of the reaction, to obtain any of these products. *Under ordinary conditions, however, nitric oxide (NO) is formed.* The course of the reaction may be shown by the study of a typical example, such as the action of nitric acid of medium concentration upon zinc. The first step in the reaction consists in the formation of zinc nitrate and hydrogen:

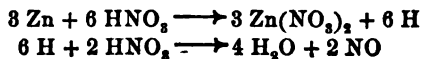


The hydrogen is not evolved as such, since it at once reacts with the nitric acid:



The products of the reaction between zinc and the acid, therefore, are zinc nitrate, water, and nitric oxide.

**Combining equations.** It is often convenient to express the reaction in a single equation. This is readily done by combining equations (1) and (2) as given above. Before the equations are combined, however, they must be modified so as to express the fact that all the hydrogen represented as formed according to equation (1) reacts with the nitric acid according to equation (2). This may be done by multiplying the first equation by 3 and the second equation by 2. The two equations will then be as follows:



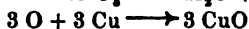
By canceling the common factor 6 H, which represents the hydrogen formed in the one reaction and consumed in the other, and then combining the equations, the following is obtained:



This complete equation has the advantage of making it possible to calculate very easily the proportions in which the various substances enter into the reaction or are formed in it. It is unsatisfactory in that it does not give full information about the way in which the reaction takes place. For example, it does not suggest that hydrogen is at first formed, and subsequently transformed into water. It is always much more important to remember the steps in a chemical reaction than to remember the equation expressing the complete action, for if these steps are understood, the complete equation is easily obtained in the manner just described.

(b) *Metals occurring below hydrogen in the electrochemical series.* Those metals occurring below hydrogen in the electrochemical series, when acted upon by nitric acid, are first oxidized to the corresponding oxides. The acid is thereby decomposed into a compound having a lower percentage of oxygen, such as nitrous acid; or it may form water and one or more of the oxides of nitrogen. The oxide of the metal, with one or two exceptions, dissolves in the acid, forming the corresponding nitrate and water.

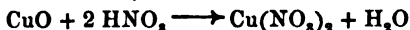
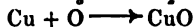
The course of the reaction may best be shown by a study of some typical examples. When moderately dilute nitric acid (density, 1.2) acts upon copper, the reaction may be expressed by the following equations:



By canceling the factors 3 O and 3 CuO, representing substances formed in one reaction and used up in another, and combining these three equations, the following equation is obtained:



If *concentrated* acid is used in place of dilute, nitrogen dioxide is liberated, as shown in the following equations:

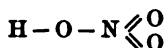


Combining these into a single equation, we obtain the following:

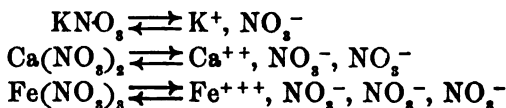


**Uses of nitric acid.** Nitric acid is used in very large quantities in the manufacture of explosives, of celluloid, and of dyes. It is a very important reagent in chemical laboratories.

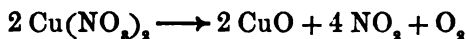
**Structural formula of hydrogen nitrate.** Since hydrogen nitrate is largely ionized in aqueous solution, it is evident that in dealing with such solutions we have to do not so much with the nitrate itself as with the ions which it forms, namely  $\text{H}^+$  and  $\text{NO}_3^-$ . The reactions of the pure compound, on the other hand, indicate that the atoms present in the molecule are combined as represented in the following structural formula:



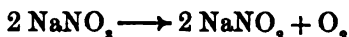
**Salts of nitric acid; the nitrates.** The salts of nitric acid are called *nitrates*. They can be obtained by the general method used for preparing salts, such as the action of nitric acid upon the metals themselves, or upon their oxides or hydroxides. Some of these, especially sodium nitrate and potassium nitrate, are found in nature. The nitrates of most of the metals are white solids. The nitrate of copper is blue, that of nickel is green, while cobalt nitrate is cherry-red. All the normal nitrates are soluble in water and form the ions  $\text{M}^+$  and  $\text{NO}_3^-$ , in which M represents the metal. Thus, potassium, calcium, and iron nitrates ionize as represented by the following equations:



When heated, the nitrates undergo decomposition. As a rule, the metal is left in the form of the oxide, while oxygen and oxides of nitrogen are evolved. Thus, when copper nitrate is heated, the blue color of the nitrate gradually gives way to the black color of copper oxide, while the evolution of nitrogen dioxide is indicated by the reddish color of the evolved gas:

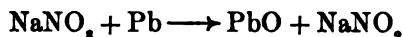


In the case of a few of the nitrates, however, oxygen alone is evolved. Thus sodium nitrate, when heated, forms sodium nitrite ( $\text{NaNO}_2$ ) and oxygen:

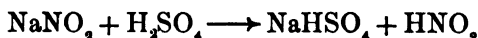


The nitrates have various uses. Large quantities of sodium nitrate are exported from Chile to different countries, where it is used in the preparation of nitric acid and in the manufacture of fertilizers. In European countries calcium nitrate ( $\text{Ca}(\text{NO}_3)_2$ ), prepared by neutralizing the dilute solution of nitric acid obtained by the Birkeland and Eyde process (p. 262) with lime ( $\text{CaO}$ ), is coming to be used as a fertilizer, under the name *air salt peter*.

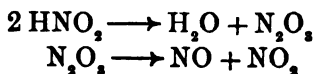
**Nitrous acid ( $\text{HNO}_2$ ).** While sodium nitrate may be decomposed by heat into sodium nitrite and oxygen, a high temperature is required to effect the change. The formation of the nitrite takes place much more readily if the nitrate is mixed with a mild reducing agent, such as lead, before it is heated:



On treating the resulting mass with water, the nitrite dissolves and may be filtered from the insoluble lead oxide. When the resulting solution is evaporated, the nitrite is obtained in the form of a white solid. This compound is the sodium salt of nitrous acid. When this is treated with sulfuric acid, therefore, we should expect to have nitrous acid liberated:



When the reaction is carried out, however, we obtain not nitrous acid but a mixture of nitric oxide and nitrogen dioxide. Nitrous acid is at first formed, but, being unstable, it decomposes at once into water and nitrogen trioxide ( $\text{N}_2\text{O}_3$ ), the latter compound in turn yielding nitric oxide and nitrogen dioxide. These reactions are expressed in the following equations:



When a mixture of nitric oxide and nitrogen dioxide is passed into cold water, the resulting liquid contains a slight amount of nitrous acid, but this soon decomposes, forming nitric acid, as represented in the following equation:

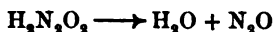


Inasmuch as nitrous acid combines with oxygen, forming nitric acid, it acts as a reducing agent in the presence of substances that readily yield oxygen. On the other hand, in the presence of a substance having a strong affinity for oxygen, nitrous acid acts as an oxidizing agent, decomposing as represented in the following equation:



**Salts of nitrous acid; the nitrites.** While nitrous acid itself is very unstable, its salts, the nitrites, are comparatively stable. Like the nitrates, most of these salts are solids and soluble in water. The nitrites of potassium and of sodium are common reagents in the chemical laboratory.

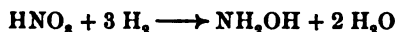
**Hyponitrous acid.** Just as nitric acid, under the influence of reducing agents, gives up oxygen, forming nitrous acid, so the latter compound, when similarly treated, loses oxygen, forming a compound known as hyponitrous acid. This compound contains hydrogen, nitrogen, and oxygen in the proportion represented by the formula  $\text{HNO}$ . The determination of the molecular weight of the compound, however, shows that it is just double that represented by the formula  $\text{HNO}$ . Since the formula is always intended to represent the composition of the molecule, we must assign to hyponitrous acid the formula  $\text{H}_2\text{N}_2\text{O}_2$ . This acid, while very unstable, has nevertheless been obtained in the form of white crystals. These dissolve in water, forming a solution of the acid, which, however, soon decomposes into water and nitrous oxide:



The salts of the acid are known as hyponitrites. A number of these have been prepared. The silver salt is a yellow solid rather easily obtained, since it is only slightly soluble in water.

**Hydroxylamine ( $\text{NH}_2\text{OH}$ ).** This compound may be regarded as ammonia in which an atom of hydrogen has been replaced by the radical  $\text{OH}$ . The name *hydroxylamine* indicates the presence of the hydroxyl group, as well

as of the amino group ( $\text{NH}_2$ ). Hydroxylamine was first obtained in dilute solution in 1865, but the compound was not isolated in a pure state until 1891, when de Bruyn obtained it in the form of white needles melting at  $38^\circ$ . It is formed by the action of hydrogen on nitric acid:



Hydroxylamine resembles ammonia in being soluble in water, combining with it to form the base  $(\text{NH}_2\text{OH})\text{OH}$ . This base, however, is much less ionized and therefore weaker than ammonium hydroxide. By the action of strong acids the corresponding salts may be obtained. Thus, with hydrochloric acid there is formed the chloride  $(\text{NH}_2\text{OH})\text{Cl}$ . These salts are more stable than the free body and are therefore more largely used. It is a strong reducing agent, its reducing properties being much more marked than those of ammonia. Its chief importance lies in its reactions with certain types of carbon compounds.

### COMPOUNDS OF NITROGEN WITH OXYGEN

The names and formulas of the oxides of nitrogen are as follows:

Nitrous oxide (hyponitrous anhydride) ( $\text{N}_2\text{O}$ ), a colorless gas.

Nitric oxide ( $\text{NO}$ ), a colorless gas.

Nitrogen dioxide ( $\text{NO}_2$ ), a gas, deep reddish-brown in color.

Nitrogen trioxide (nitrous anhydride) ( $\text{N}_2\text{O}_3$ ) exists only at low temperatures, both in liquid and solid form.

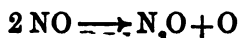
Nitrogen tetroxide ( $\text{N}_2\text{O}_4$ ), a nearly colorless liquid.

Nitrogen pentoxide (nitric anhydride) ( $\text{N}_2\text{O}_5$ ), a white crystalline solid.

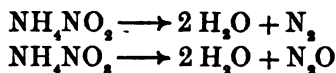
Nitrogen hexoxide ( $\text{N}_2\text{O}_6$ ), an unstable, greenish solid.

**Nitrous oxide (laughing gas) ( $\text{N}_2\text{O}$ ).** Nitrous oxide was first prepared by Priestley in 1772. Davy determined its composition in 1800 and was the first to point out that the gas renders one temporarily unconscious when it is inhaled.

**Preparation.** Nitrous oxide can be prepared by the action of suitable reducing agents upon nitric acid, as well as upon nitric oxide. Priestley first obtained it from this latter compound by the reducing action of iron:



The most convenient method for its preparation consists in heating ammonium nitrate. Just as ammonium nitrite, when heated, yields water and nitrogen (p. 152), so ammonium nitrate decomposes in a similar way, forming water and nitrous oxide. The similarity between the two reactions is shown in the following equations:



The decomposition is effected by heating the ammonium nitrate in a flask such as that used in the preparation of oxygen (Fig. 6, p. 23). The nitrous oxide is evolved and may be collected over warm water, since it is noticeably soluble in cold water.

**Properties.** Nitrous oxide is a colorless gas and has a faint odor. Its solution has a slightly sweetish taste. It is 1.53 times as heavy as air, 1 l. of it weighing 1.9777 g. Its critical temperature is  $38.8^\circ$  and its critical pressure 7.5 atmospheres. Liquid nitrous oxide is colorless and boils at  $-89.4^\circ$ .

Chemically, nitrous oxide is characterized by the ease with which it decomposes into free nitrogen and oxygen. It is therefore a good oxidizing agent. Such substances as carbon, iron, and phosphorus, when ignited and introduced into jars of the gas, burn with brilliancy, forming oxides and nitrogen. When inhaled, it produces a kind of hysteria (hence the name *laughing gas*) and even unconsciousness and insensibility to pain. It has long been used as an anesthetic for minor surgical operations, such as those of dentistry.

**Nitric oxide (NO).** This gas was discovered by Van Helmont and was used by Priestley in the analysis of air (p. 169).

**Preparation.** Nitric oxide is most readily prepared by the action of nitric acid (density, 1.2) upon certain metals, such as copper (p. 267).

The metal is placed in a flask *A* (Fig. 87) and the acid slowly added through the funnel tube *B*. The gas escapes through *C* and is collected over water. The gas at first evolved combines with the oxygen of the air contained in the flask to form the reddish-brown nitrogen dioxide, but this is absorbed as it bubbles through the water.

**Properties.** Nitric oxide is a colorless gas slightly heavier than air. It is very much more difficult to liquefy than nitrous oxide. Its critical temperature is  $-98.5^{\circ}$  and its critical pressure 71.2 atmospheres. The liquid boils at  $-153^{\circ}$ . Nitric oxide is a much more stable compound than nitrous oxide; nevertheless, it can

be decomposed into its elements without difficulty. If a bit of phosphorus is barely ignited and at once introduced into a jar of the gas, the flame is extinguished. On the other hand, if the phosphorus is first heated until vigorous combustion ensues, and is then introduced into the gas, the combustion continues with great brilliancy. One of the most characteristic properties of nitric oxide is its conduct toward oxygen. When brought in contact with oxygen or air, it forms nitrogen dioxide ( $\text{NO}_2$ ).

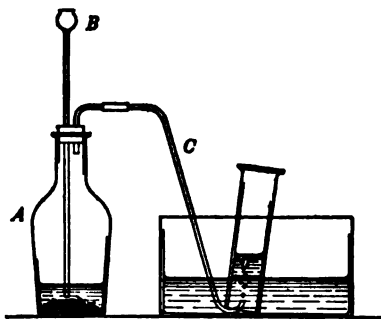
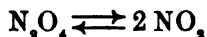


FIG. 87

**Nitrogen dioxide ( $\text{NO}_2$ ) and nitrogen tetroxide ( $\text{N}_2\text{O}_4$ ).** Since these two compounds are very closely related, it is convenient to discuss them together. We have seen that nitrogen dioxide is formed by heating copper nitrate (p. 268), as well as by the union of nitric oxide and oxygen. Either of these reactions serves as a convenient method for its preparation. When the reddish-brown gas so obtained is cooled, the color gradually fades and a faintly yellow liquid forms, which boils at about  $26^{\circ}$ . On further cooling, the liquid condenses to an almost colorless solid melting at  $-10^{\circ}$ . This solid is pure nitrogen tetroxide ( $\text{N}_2\text{O}_4$ ). As the temperature rises, the reverse change takes place, the tetroxide gradually changing back into the deeply colored gaseous dioxide. At  $150^{\circ}$  the change into the dioxide is complete. Between these extremes of temperature the gas

consists of a mixture of the two compounds in equilibrium with each other:



The mixture is generally referred to, however, as nitrogen dioxide or nitrogen peroxide. At still higher temperatures the dioxide is broken up into nitric oxide and oxygen. From what has been said it is evident that whenever either the dioxide or the tetroxide is generated at ordinary temperatures, a portion of the one compound immediately changes into the other, so that we are really dealing with a mixture of the two.

Compounds related to each other as nitrogen dioxide is related to nitrogen tetroxide are termed *polymeric compounds*, or simply *polymers*. Such compounds have the same percentage composition but different molecular weights.

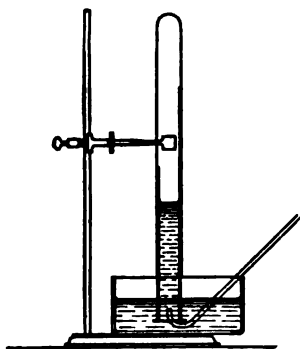
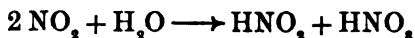


Fig. 88

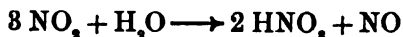
**Experimental details.** The formation of nitrogen dioxide from nitric oxide and oxygen, together with the reaction between the dioxide and water, may be shown as follows: A tube is filled with water and inverted in a vessel of water, as shown in Fig. 88. The tube is then nearly filled with nitric oxide, after which oxygen is admitted, a few bubbles at a time. As each bubble enters the tube, the deep reddish-brown dioxide forms. After a few

moments the color fades, owing to the fact that the dioxide reacts with the water, which at the same time rises in the tube to take the place of the gas so removed. It will be recalled (p. 169) that by a similar method Priestley originally determined what he called the "goodness of air."

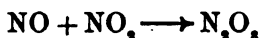
The reaction which takes place between the dioxide and water depends upon the temperature. In cold water both nitric and nitrous acids form:



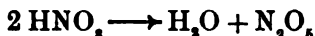
At a higher temperature the nitrous acid decomposes as fast as formed, and the reaction may be represented as follows:



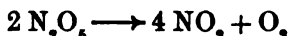
**Nitrogen trioxide ( $\text{N}_2\text{O}_3$ ).** When a mixture of equal volumes of nitric oxide and nitrogen dioxide is cooled, there is obtained at first a blue liquid, which, at a still lower temperature, freezes to a solid. The liquid, as well as the solid, is generally regarded as nitrogen trioxide:



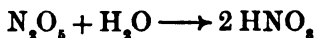
**Nitrogen pentoxide ( $\text{N}_2\text{O}_5$ ).** This oxide is formed when nitric acid is treated with a strong dehydrating agent, such as phosphorus pentoxide:



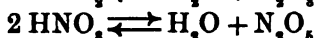
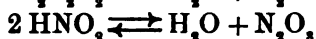
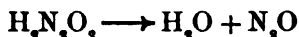
Nitrogen pentoxide is a white crystalline solid melting at  $29.5^\circ$ . It readily decomposes into nitrogen dioxide and oxygen:



It combines energetically with water, forming nitric acid:



**Anhydrides.** From the statements made it will be seen that each of the oxygen acids of nitrogen decomposes into water and an oxide of nitrogen, as represented in the following equations:



In the case of hyponitrous acid and nitrous acid this decomposition takes place spontaneously, while with nitric acid a dehydrating agent is necessary to bring about the reaction. Nearly all acids containing oxygen undergo a similar reaction, and the oxides resulting are termed *acid anhydrides*. Thus nitrogen pentoxide is the anhydride of nitric acid and is often called *nitric anhydride*. Similarly,  $\text{N}_2\text{O}$  and  $\text{N}_2\text{O}_3$  are the anhydrides of hyponitrous acid and nitrous acid respectively. The decomposition of an acid into water and the corresponding anhydride is, as a rule, a reversible reaction. Thus the anhydrides of nitrous acid and nitric acid unite with water to form the corresponding acids.

**The decomposition of nitrogenous organic matter.** The protein matter occurring in plants and animals may be decomposed in a number of ways, the most important of which are the following:

1. *By the action of microorganisms.* Experiments have shown that organic matter will decay only in the presence of certain microorganisms, which in some way assist in its decomposition. In this process a part of the nitrogen is evolved as free nitrogen, while other portions are converted into ammonia, nitrites, or nitrates.

2. *By the action of heat.* When heated in the absence of air, protein matter undergoes complicated changes, in which a portion of the nitrogen is evolved in the form of ammonia.

3. *By the action of acids or bases.* When heated to a high temperature with concentrated sulfuric acid, the nitrogen present in organic matter is converted into ammonia. Since the ammonia formed in this process can readily be estimated, the reaction is used to ascertain the amount of nitrogen in organic matter, such as foods and fertilizers. This way of determining nitrogen is known as the *Kjeldahl* method. Strong alkalies have a similar action on nitrogen products, the nitrogen being evolved in the form of ammonia.

**The cycle of nitrogen.** The nitrogen present in the soil in the form of nitrates is taken up by plants and built into protein matter. This matter undergoes a series of changes which finally result in restoring to the soil the nitrogenous matter originally extracted from it. The cycle through which the nitrogen passes may be illustrated in a general way by the diagram (Fig. 89).

The nitrogen in the nitrates *A* of the soil is built into plant protein *B*, and this in turn into animal protein *C*. During life the nitrogen assimilated by animals is largely eliminated in the form of urea (p. 884), which decomposes into ammonia, as indicated in the figure. After death the tissue *D* undergoes decay, largely changing into ammonia and free nitrogen *E*. The latter escapes into the air, while the ammonia is absorbed by water and ultimately, through the action of certain microorganisms,

changes into nitrites *F*, and finally into nitrates *A*. The free nitrogen evolved in the decay of the dead tissue may be built up again into compounds through the action of the microorganisms present on the roots of certain plants.

It will be recalled that the presence of organic matter in water indicates that the water has been polluted and is unfit for sanitary purposes. This organic matter is extremely complex in character, and there is no simple way of determining its quantity and nature, especially when it is present in small

amounts. On the other hand, very delicate tests are known for its decomposition products, — namely, ammonia, nitrites, and nitrates, — and these compounds are not likely to be present unless derived from organic matter. In making an analysis of water, therefore, the percentages of these products are determined, and from the results conclusions are drawn as to the purity of the water.

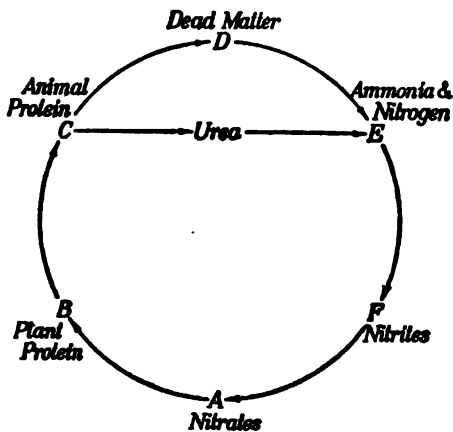


FIG. 89

### QUESTIONS

1. Mention different reactions so far studied in which a catalytic agent is used.
2. Give the relative advantages of the different methods for preparing nitric acid.
3. (a) What is a radical? (b) Illustrate by examples taken from this chapter. (c) How can you tell the valence of a radical?
4. Concentrated sulfuric acid has a strong affinity for water. Why not dry the ammonia prepared as illustrated in Fig. 81 with sulfuric acid in place of lime?

5. Contrast the effect of heating aqueous solutions of ammonia and of hydrogen chloride.

6. Mention two general methods for the preparation of nitrides. Does either one of these methods serve to prepare ammonia from the nitrogen of the atmosphere?

7. What different constituents are present in aqua ammonia?

8. If hydrogen is prepared and passed into nitric acid, there is little, if any, action. On the other hand, if the hydrogen is generated in contact with nitric acid, the acid is decomposed. Explain.

9. When carbon is burned in an atmosphere of nitrous oxide, considerably more heat is evolved than when it is burned in pure oxygen. Explain.

### PROBLEMS

1. What weight of ammonia is necessary for preparing 1 l. of a normal solution of ammonium hydroxide?

2. Calculate the number of grams of ammonium chloride and sodium hydroxide necessary for the preparation of sufficient ammonia to saturate 10 l. of water at  $0^{\circ}$  and 760 mm.

3. One liter of a normal solution of ammonium hydroxide is added to 1 l. of a normal solution of nitric acid and the resulting solution evaporated to dryness. Calculate the weight of the residue.

4. Assuming that the yield obtained is 90 per cent of the theoretical yield, what weights of each of the raw materials would be required to make 100 kg. of the concentrated nitric acid of commerce by the sodium nitrate method?

5. 100 cc. of the concentrated nitric acid of commerce was added to 30 g. of copper. When the reaction ceased the liquid present was evaporated just to dryness. (a) What was the composition of the residue? (b) Calculate its weight.

6. Which of the oxides of nitrogen contains the greatest percentage of nitrogen? Calculate this percentage.

7. The ordinary aqua ammonia of the druggist must contain not less than 9.5 per cent, nor more than 10.5 per cent by weight of  $\text{NH}_3$  in order to meet the law's requirements. A sample secured from a druggist gave the following results: 4.75 g. of the sample required 28 cc. of a normal solution of sulfuric acid to neutralize it. Does the sample conform with the law?

## CHAPTER XVIII

### EQUILIBRIUM

**Introduction.** The general idea of equilibrium as a balance between two changes opposing each other has been developed in a number of instances in the foregoing pages. It is desirable to bring these cases together to see if we can gain a more systematic view of the underlying causes that result in equilibrium.

**Physical equilibrium.** Many examples of purely physical equilibrium have already been described. Thus the freezing point of a liquid has been defined as the temperature at which the liquid and solid remain unchanged in contact with each other. The rate at which the solid melts is just balanced by the rate at which the liquid freezes. The unchanging vapor pressure at a given temperature is due to the fact that the rate at which molecules leave the liquid is just balanced by the rate of their return. Saturation is reached when the rate at which a solid or a gas dissolves is just compensated by the rate of its deposit or escape from solution.

In all these cases, *when equilibrium is reached, the condition is not one of rest but of motion*; the number of molecules taking part in one change is just equal to the number taking part in an opposite change.

**Chemical equilibrium.** When chemical action takes place between two substances, it often happens that the action is incomplete, some of both materials apparently failing to take part in the reaction. Experiment has shown that in these cases there results an equilibrium very similar to those of physical equilibrium just enumerated. For an understanding of the conditions which produce such an equilibrium, it will be necessary first to make a study of the factors influencing the speed of reactions which reach completion.

**Factors which influence the speed of reactions.** By the *speed* of a reaction is meant the quantity of material undergoing transformation in a suitable unit of time, such as a second, a minute, or an hour. Quite a number of factors are involved in producing this speed.

1. *Affinity.* The specific attraction between the reacting substances, which we call chemical affinity, is of fundamental importance. Some substances, such as fluorine and oxygen, will not unite at all. Under certain conditions others, as hydrogen and oxygen, act upon each other with great rapidity. Other things being equal, *the greater the affinity between the substances the greater the speed of their reaction.* The speed may therefore be employed as a measure of the affinity.

2. *Temperature.* A rise in temperature always greatly increases the speed of a reaction. As a rough approximation Ostwald has estimated that a rise of  $10^{\circ}$  about doubles the speed. If, therefore, a reaction is proceeding at a given speed at  $0^{\circ}$ , it will go twice as fast at  $10^{\circ}$  and four times as fast at  $20^{\circ}$ . At  $100^{\circ}$  its speed will be 1024 times as great as at  $0^{\circ}$ . Reactions whose speed is imperceptible at ordinary temperatures (for example, the oxidation of coal) may therefore become very rapid at a temperature within the reach of a Bunsen burner. On the other hand, we can greatly retard a reaction by keeping the material cold, as when we put food in cold storage.

3. *Catalysis.* The change in the speed of a reaction due to catalytic agents has been commented upon in several instances, as in the decomposition of potassium chlorate in the presence of manganese dioxide. It has been found that the speed of the great majority of reactions can be modified by some suitable catalyzer, and that it may be either hastened or retarded in this way. The effect produced by an accelerating catalyzer is the same as if the reaction were to be carried on at a higher temperature so that it is often more economical to employ a suitable catalyzer than to be at the expense of maintaining the higher temperature. Since the catalyzer merely changes the speed of

reaction, and does not add any energy to the reacting bodies, it cannot bring about a reaction which does not take place by itself; for example, it cannot maintain an endothermic reaction.

Without doubt catalyzers exert their influence in a variety of ways. Some appear to owe their efficiency to the very large surface which they present to the reacting mixture. Some strongly absorb one or both of the substances taking part in the reaction and in this way bring about very marked changes in concentration. Still others form a definite, but unstable, compound which later undergoes decomposition and restores the catalyzer to act over again.

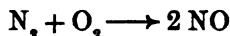
4. *Concentration.* Since reactions take place between individual molecules, and since these cannot act upon each other at a distance, it will be seen that any condition which increases the frequency of their meeting will promote the speed of reaction. The more molecules there are in a given space the faster the reaction will proceed, so that *the molecular concentration will greatly affect the speed of reaction.* In cases where a gas is one of the reacting bodies, the pressure under which the gas is maintained will have great influence, not because of any physical effect of pressure, but because *the pressure determines the concentration of the gas*, Boyle's law reminding us that when the pressure is doubled, the same number of molecules is crowded into half the space.

5. *Solution.* Solution promotes the speed of reaction in another way. We think of the molecules of a solid as held together by very considerable forces called cohesive forces. The solvent overcomes these forces, giving the liberated molecules that much more energy with which to enter into chemical reactions. Being pulled apart and set moving through the solvent, the molecules will have much more frequent meetings with other dissolved molecules than if they had remained on the surface of the solid. This whole description is sometimes expressed by saying that the solvent creates an *external field of force* that acts in opposition to the cohesive forces of the solid.

**The law of mass action.** Of the five factors just enumerated, the effect of concentration upon the speed is most easily measured. As early as the beginning of the nineteenth century, Berthollet made important measurements of this kind, but it was not until 1867 that the relation of concentration to the speed of a reaction was definitely formulated. In this year the Norwegian scientists Guldberg and Waage published the results of their investigations in the form of the *law of mass action*, which states that the speed of a reaction is proportional to the molecular concentrations of each of the reacting substances.

Since the speed depends upon the frequency of meeting of molecules, it is clear that by *concentration* is meant not the weight in grams per liter but the number of gram-molecular weights per liter.

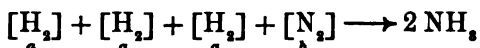
To illustrate the meaning of this law, let us take the reaction expressed by the equation



Let  $[a]$  and  $[b]$  be the *molecular concentrations* of the nitrogen and oxygen at the outset. The speed will be *proportional* to the number of nitrogen molecules in unit volume  $[a]$ , and also to that of the oxygen molecules  $[b]$ . In accordance with the simple principles of algebra it will therefore be *proportional* to the product  $[a] \times [b]$ . In *actual magnitude* the speed will also depend upon the temperature, the presence of catalyzers, the affinities of the reacting substances, and the units employed in the measurement. At a given temperature and with a given set of units, all these influences are constant in value, and we may designate their combined effect by the constant  $k$ , which is called the *affinity constant* at that temperature. We shall then have the equation

$$\text{Speed} = [a] \times [b] \times k$$

In the formation of ammonia from its elements, where more than one molecule of a given kind enters into the reaction, the full equation is

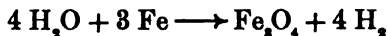


Evidently the speed is not proportional merely to  $[a]$ , the concentration of the hydrogen, but to the product  $[a] \times [a] \times [a] \times [b]$ , so that we have the equation

$$\text{Speed} = [a]^3 \times [b] \times k$$

**Illustration.** The student is likely to consider these equations hard to understand, while in everyday life he would understand a parallel instance almost as a matter of course. For example, the speed of a man walking is *proportional* to the length of his step, and also *proportional* to the rapidity of his steps. It is therefore *proportional* to the product of the two. To say that it is *equal* to this product would have no meaning until we agree upon a unit for length (say a foot) and for rapidity (say number of steps per minute). We can then say the speed = length of step  $\times$  rapidity of step  $\times$  a constant made up of feet and minutes. If he slips back a few inches in making each step, this will still further modify the size of the constant.

**Active mass.** A reaction taking place in a mixture of gases or in solution is said to be *homogeneous*, because the concentration of each component is the same in every part of the mixture. The concentration of each can be stated in gram-molecules per liter. When a solid is acted upon by a gas, as in the reaction of steam upon iron, or by a liquid, as when hydrochloric acid acts upon zinc, the reaction is said to be *heterogeneous*, because the materials are not mixed with each other in even concentration. In the reaction expressed by the equation

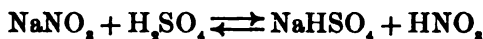


we have no difficulty in defining the concentration of the steam and in seeing that every molecule of it is available for the reaction. With the iron the case is quite different. Only those molecules forming the surface of the solid, or given off as vapor, can have any effect upon the velocity of the reaction at a given time, and in either case the effect will be practically, though not accurately, constant. *That portion of a substance which is available for a reaction at a given time is called its active mass*, and it is with the concentration of the active mass that the law of mass action is concerned. The best we can do in regard to the

before, by introducing a little sulfuric acid. When the experiment is carefully conducted, the percentage of the ammonia by volume is the same in each case, showing that the same equilibrium is reached whether the reaction is conducted in one direction or in the other.

If sulfuric acid is added at the outset of the first experiment, the contraction continues as long as the sparks are passed through the mixture, for the ammonia is removed as fast as it is formed, and no equilibrium can be reached.

**I. Influence of concentration on equilibrium.** Since the speed of any reaction depends upon the concentration of every substance taking part in the reaction, it is clear that the point of equilibrium will also depend upon the concentration of each of the components of the two opposing reactions. As an example, let us study the reaction employed in preparing nitric acid; and let us assume that all four of the substances concerned are present in a state of equilibrium represented in the equation



The speed of the reaction of sodium nitrate with sulfuric acid is stated in the equation

$$\text{Speed} = \text{Con.} [\text{NaNO}_3] \times \text{Con.} [\text{H}_2\text{SO}_4] \times k$$

in which  $k$  is the affinity constant of the reaction.

The speed of the opposing reaction is expressed in the equation

$$\text{Speed} = \text{Con.} [\text{NaHSO}_4] \times \text{Con.} [\text{HNO}_3] \times k'$$

in which  $k'$  is the affinity constant of this opposite reaction. *At equilibrium these two speeds are equal.* So we may write

$$\begin{aligned} \text{Con.} [\text{NaNO}_3] \times \text{Con.} [\text{H}_2\text{SO}_4] \times k \\ = \text{Con.} [\text{NaHSO}_4] \times \text{Con.} [\text{HNO}_3] \times k' \end{aligned}$$

$$\text{or} \quad \frac{\text{Con.} [\text{NaNO}_3] \times \text{Con.} [\text{H}_2\text{SO}_4]}{\text{Con.} [\text{NaHSO}_4] \times \text{Con.} [\text{HNO}_3]} = \frac{k'}{k} = K$$

For since  $k'$  and  $k$  are both constants, the quotient of one by the other is also a constant which we may designate by  $K$ . It is called the *equilibrium constant*.

**The equilibrium constant.** As is suggested by the name, the equilibrium constant is an unchanging number (at a given temperature) which is perfectly definite for any given reaction, no matter what concentrations of materials may be present. If we can find a method for measuring the four concentrations in the equation at equilibrium, we can at once calculate the value of this constant. For example, let us suppose that at equilibrium and at 20° we can show that, *expressed in gram-molecules per liter*, the following values of concentration are true:

$$\begin{array}{ll} \text{Con. [NaNO}_3\text{]} = 0.6 & \text{Con. [NaHSO}_4\text{]} = 0.9 \\ \text{Con. [H}_2\text{SO}_4\text{]} = 0.8 & \text{Con. [HNO}_3\text{]} = 1.1 \end{array}$$

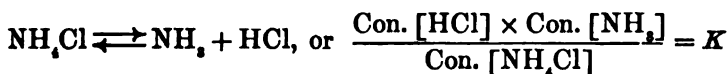
If we substitute these values in our equilibrium equation, we have

$$\frac{[0.6] \times [0.8]}{[0.9] \times [1.1]} = K = 0.485$$

**Effect of changes in concentration on equilibrium.** If we bring together these four substances in some proportion other than that required by the constant  $K$ , the reaction will go on in one or the other direction until the four concentrations attain values that once more give  $K = 0.485$ .

If we greatly increase the concentration of some one of the components (say the sulfuric acid), then all the other concentrations must change. It will be seen that in this case the concentration of  $\text{NaNO}_3$  must become less, and that of both  $\text{NaHSO}_4$  and  $\text{HNO}_3$  greater, to bring the quotient back to the same old value for  $K = 0.485$ . In other words, we cause the equilibrium to shift towards the right. *We often add a large excess of one component in this way to push the reaction as near to completion as possible.*

**Other types of equilibrium.** Of course there are not always four compounds present at a state of equilibrium. We often have a reaction of the type expressed in the equation

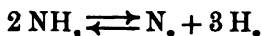


The reversible reaction  $2 \text{SO}_2 + \text{O}_2 \rightleftharpoons 2 \text{SO}_3$  leads to the concentration equation

$$\frac{\text{Con. } [\text{SO}_3]^2 \times \text{Con. } [\text{O}_2]}{\text{Con. } [\text{SO}_2]^2} = K$$

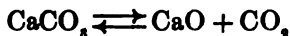
The principles just developed may be applied to all such reactions without difficulty, and with much profit.

**II. Influence of pressure on equilibrium.** The reactions in which gases are concerned are often attended by large changes in volume. For example, in the reaction between sulfur dioxide ( $\text{SO}_2$ ) and oxygen ( $\text{O}_2$ ) just given, there is a decrease in the volume in the ratio of 3:2; while in the reaction



there is an expansion in the ratio 1:2. When a state of equilibrium has been reached in any such case, a change in the pressure has a great effect upon the point of equilibrium. *Increase of pressure will shift the point of equilibrium toward the side of the equation having the smaller volume.* In the last equation given, increase of pressure will favor the formation of ammonia from a mixture of hydrogen and nitrogen. We have seen that this is true in the Haber process (p. 250).

**Reactions of dissociation.** There is a type of chemical reaction, many examples of which we shall meet, in which a solid decomposes or *dissociates* into a second solid and a gas. Thus the carbonates when heated yield an oxide of the metal and carbon dioxide:



We may express this decomposition in a concentration equation thus:

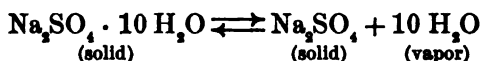
$$\frac{\text{Con. } [\text{CaO}] \times \text{Con. } [\text{CO}_2]}{\text{Con. } [\text{CaCO}_3]} = k$$

But both  $\text{CaO}$  and  $\text{CaCO}_3$  are *solids*, and their active masses or concentrations may each be regarded as constant and may be designated by  $k'$  and  $k''$ . We will then have

$$\frac{k' \times \text{Con. } [\text{CO}_2]}{k''} = k, \text{ or } \text{Con. } [\text{CO}_2] = \frac{k \times k'}{k''} = K$$

In other words, the concentration of  $\text{CO}_2$  in equilibrium with  $\text{CaO}$  and  $\text{CaCO}_3$  is *constant* (at a given temperature). But the concentration of a gas is proportional to its pressure; so we may say that at a given temperature the *pressure* of  $\text{CO}_2$  in contact with  $\text{CaO}$  and  $\text{CaCO}_3$  is *constant*. This constant pressure, due to the gas formed, is called the *dissociation pressure* of the compound from which the gas is formed.

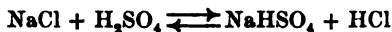
**Efflorescence of hydrates.** An entirely similar case is presented by many hydrated salts which tend to lose water (as vapor) and form a lower hydrate or an anhydrous salt, thus:



At a definite temperature the salt will give off water vapor until equilibrium is reached with the two solids concerned in the reaction. In the open air, where the water vapor can continually escape, no equilibrium can be reached, *unless the partial pressure of the water vapor present in the air is equal to the dissociation pressure of the hydrate*. If this partial pressure is *equal to* (or *greater than*) the dissociation pressure of the hydrate, no dissociation occurs. If it is *less*, the hydrate steadily loses water vapor to the air, and usually crumbles to powder consisting of the anhydrous salt or a lower hydrate. Loss of water in this way is called *efflorescence*, and the hydrate is said to be *efflorescent* in air.

**III. Influence of temperature on equilibrium.** Since each of the two opposing reactions in an equilibrium is the reverse of the other, it is evident that if one reaction evolves heat, the other one must absorb an equal amount of heat. At equilibrium the heat given out by the one reaction is exactly absorbed by the other. If now we add heat from an outside source we will help along the heat-absorbing reaction, whereas if we cool the mixture we will aid the heat-evolving reaction. Consequently a change in temperature will have a marked effect in changing the point of equilibrium, and our equilibrium constant will have a different value for each point of temperature.

**Illustration.** These statements may be easily tested by two experiments suggested by the equilibrium equation



When sodium chloride is treated with moderately concentrated sulfuric acid, there is at the outset a very considerable evolution of heat, as shown by a thermometer introduced into the solution. On the other hand, when sodium hydrogen sulfate is treated with concentrated hydrochloric acid, there is a corresponding cooling of the solution, which is often sufficient to cause the beaker containing the solution to freeze fast to a wet block of wood on which it is placed.

**Theorem of Le Chatelier.** The effect of changes in temperature and in pressure upon chemical equilibrium are but illustrations of a far-reaching generalization known as the theorem of Le Chatelier. This theorem deals with changes in an equilibrium of *any sort*, produced not only by changes in pressure or temperature, but by forces of *any kind* brought to bear upon the equilibrium. The theorem states that the equilibrium will always move in such a way as to diminish the intensity of the added force. Thus, if we increase the pressure, the equilibrium moves toward a state of smaller volume and so diminishes the intensity of the pressure; if we add heat it moves in such a direction that the heat-absorbing reaction absorbs this heat. In general words we may state the *Theorem of Le Chatelier* as follows: *If we bring an additional force to bear upon an equilibrium, the point of equilibrium will shift in such a direction as to diminish the intensity of the force so applied.*

**Illustration of combined effects.** In the following chapter we shall see that the manufacture of sulfuric acid depends upon the reaction expressed in the equilibrium equation

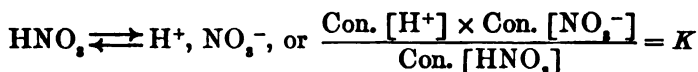


The industrial problem is to push the yield as far as possible towards the production of  $\text{SO}_3$  and at a low cost. It will be necessary to take into account the following considerations:

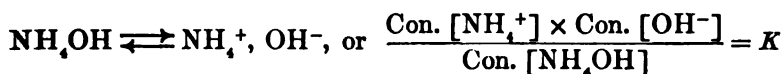
(1) The law of mass action suggests that we increase the  $\text{O}_2$  much beyond the quantity required by the equation, because the

oxygen is furnished by the air and is cheap. (2) There is a decrease in volume in the reaction, so we should apply pressure to the system if this is at all economical. (3) Heat is evolved, and if the reaction goes at all fast, the rise in temperature will diminish the yield because the reverse reaction will be stimulated. Therefore we should cool the reaction mixture by suitable methods. (4) But cooling will slow up the reaction at an expense in time. Therefore we should seek a catalyzer that will speed up the reaction at a lower temperature (p. 280).

**Equilibrium and ionization.** The type of equilibrium that we shall meet more often than any other is that of an electrolyte in solution in equilibrium with its ions. With nitric acid the ionization is expressed by the equation



Similarly, for ammonium hydroxide the equilibrium equation is



It should be noted that the concentration equation is always arranged in such a way as to place the concentrations of the ions in the numerator of the fraction. In the case of an electrolyte the equilibrium constant  $K$  is usually called the *ionization constant*. For strongly ionized substances, such as strong acids and bases, as well as nearly all salts, the value of  $K$  is large, since even in normal solution these are largely ionized (p. 242). For weak electrolytes, such as ammonium hydroxide, the value of  $K$  is a very small fractional number.

**Effect of dilution on ionization.** A study of these equations will show that the effect of dilution should be to increase ionization. To make this clear, let us suppose that we start with a solution containing one gram-molecule of the electrolyte AB per liter, and that 20 per cent of it is ionized at this concentration. The concentration of the un-ionized molecules is then 0.8. The remaining 0.2

gram-molecules is dissociated into two ions, and the *gram-molecular concentration* of each of these is 0.2. This gives us the equation

$$\frac{[A^+] \times [B^-]}{[AB]} = K, \text{ or } \frac{[0.2] \times [0.2]}{[0.8]} = K = 0.05$$

Let us suppose that an additional liter of water is now added. The first effect of this will be to diminish the concentration of each ion and molecule to one half of its former value. This would give

$$\frac{[0.1] \times [0.1]}{[0.4]} = K = 0.025$$

This gives a numerical value for  $K$  of just one half of its original value. But at a given temperature  $K$  is a constant and does not change. So the numerator of the equation must increase and the denominator diminish until the original value is restored. This means that more of the molecules must pass into ionic form until the quotient reaches the original value (0.05).

This effect is just what would be expected from a kinetic point of view. Change in concentration will have little effect upon the rate at which molecules dissociate into ions, but the combination of ions into molecules will depend upon how often they chance to meet, and the more they are scattered through a large volume of solvent the less frequently will this occur.

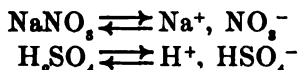
**Strong electrolytes and the law of mass action.** The equilibrium constant for weak electrolytes, such as ammonium hydroxide, remains unchanged over a wide range of concentration, and the law of mass action applies very perfectly. For reasons which are not as yet entirely clear, *this is not so with strongly ionized electrolytes*, the value of the equilibrium constant changing very considerably with the concentration. It seems probable that strong electrolytes are almost completely ionized in rather concentrated solutions, but our usual methods of measurement do not give this result.

In all such cases, as, for example, with nitric acid, the equations just explained will not apply with accuracy over any

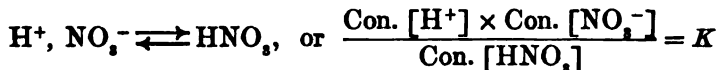
considerable range of concentration, and exact calculations cannot be based upon them. As long as a merely qualitative use is made of them, however, they can be employed without error, and it is in this way only that we shall have occasion to make use of them in our reasoning.

**Conditions for the completion of ionic reactions.** In the preparation of chemical substances, both in the laboratory and in the industries, we are usually interested in knowing under what conditions a reaction may be pushed as far as possible toward completion. Many of these reactions are carried out in solution, and it becomes of importance to inquire into the conditions favoring completion of ionic reactions. *There are three general conditions which tend to destroy equilibrium and lead to completed reactions:*

1. *The formation of an insoluble gas.* When we bring together sodium nitrate and sulfuric acid in solution, we have at the outset the two equilibria expressed in the equations

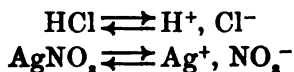


But since any positive ion is free to combine with any negative ion, the two ions  $\text{H}^+$  and  $\text{NO}_3^-$  will also come to equilibrium:

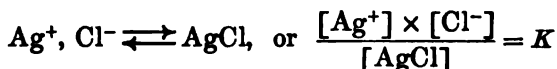


If now the solution is heated *above the boiling point of the nitric acid*, the latter distills off as fast as it is formed. More of the ions  $\text{H}^+$  and  $\text{NO}_3^-$  then combine to form molecular  $\text{HNO}_3$ , in order to maintain the value of the equilibrium constant  $K$ . This process continues until all the  $\text{HNO}_3$  which can be formed has distilled off, leaving the ions  $\text{Na}^+$  and  $\text{HSO}_4^-$ .

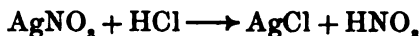
2. *The formation of a sparingly soluble solid.* When hydrogen chloride ( $\text{HCl}$ ) and silver nitrate ( $\text{AgNO}_3$ ) are brought into solution, the two equilibria result, as expressed in the following equations:



But the ions  $\text{Ag}^+$  and  $\text{Cl}^-$  will also form an equilibrium:

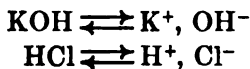


Now silver chloride ( $\text{AgCl}$ ) is very difficultly soluble in water, 1 l. dissolving only about 0.0016 g., yet the value of  $K$  is large, as is true of practically all salts. The quantity of silver chloride formed in establishing the equilibrium very quickly saturates the solution, and the excess begins to precipitate. The process will continue until the several concentrations adjust themselves to the value demanded by  $K$ . Obviously this will be when the concentration of the ions  $\text{Ag}^+$  and  $\text{Cl}^-$  is very small, practically all the silver having been precipitated in the form of silver chloride. The two ions  $\text{H}^+$  and  $\text{NO}_3^-$  are thus left alone in solution to adjust their own equilibrium, so that the reaction as expressed in the equation

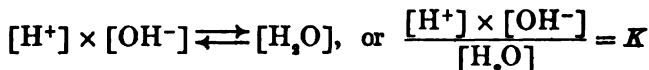


has become practically complete because of the insolubility of one of the possible equilibrium products.

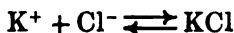
3. *The formation of very sparingly ionized molecules.* When the base  $\text{KOH}$  and the acid  $\text{HCl}$  are brought into solution, we have the equations



But the ions  $\text{H}^+$  and  $\text{OH}^-$  will set up the equilibrium



Now the rate at which water molecules ionize is extremely slow as compared with the rate of their reunion, so that *the equilibrium constant is numerically very small*, and equilibrium results when almost all the ions are in the combined form (p. 239). The only ions left in the solution, therefore, are  $\text{K}^+$  and  $\text{Cl}^-$ , which come to the equilibrium expressed in the equation



When the solution is evaporated, this equilibrium results in the formation of more and more of the salt  $\text{KCl}$ , and it is this which crystallizes from the solution when saturation is reached. The reaction is therefore practically completed, because one of the possible equilibrium products is so sparingly ionized that it restores almost none of its constituent ions to the solution. But even this small concentration of its ions,  $\text{H}^+$  and  $\text{OH}^-$ , is of very great importance under certain conditions, and this will be discussed under the topic Hydrolysis (p. 326).

### QUESTIONS

1. How many cases of equilibrium in earlier chapters can you recall?

2. What reactions can you think of that do not appear to be reversible?

3. How can you make the equilibrium  $\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4\text{OH}$  move (a) to the right? (b) to the left?

4. If you were to try to reverse the reaction  $\text{Zn} + 2\text{HCl} \rightleftharpoons \text{ZnCl}_2 + \text{H}_2$ , what methods would you employ?

5. In any equilibrium reaction, for example, in the one expressed in the equation  $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$ , would it make any difference in the final equilibrium which set of molecules you start with?

6. In solution, zinc sulfate ( $\text{ZnSO}_4$ ) and barium sulfide ( $\text{BaS}$ ) enter into double decomposition with each other. (a) Set up the equilibrium equation in terms of concentrations. (b)  $\text{BaSO}_4$  is an insoluble solid; how does this change your equation? (c)  $\text{ZnS}$  is an insoluble solid; how does this further change your equation? (d) Judging by your last equation, upon what will the final state of equilibrium depend?

7. (a) Set up a concentration equation showing the equilibrium of iron with steam. (b) Iron is a solid; how will this affect your equation? (c) Iron oxide is also a solid; how will this further affect your equation? (d) Upon what will the equilibrium finally depend?

8. Lead chloride ( $\text{PbCl}_2$ ) and lead sulfate ( $\text{PbSO}_4$ ) are insoluble solids. Suggest a probable method for preparing them.

9. By the theorem of Le Chatelier explain why air becomes hot when compressed and cold when rarefied.

## CHAPTER XIX

### SULFUR; SELENIUM; TELLURIUM; HYDROLYSIS

**History and occurrence of sulfur.** Sulfur occupied a prominent place among the few elements known to the ancients, and played an important part in the older views concerning the composition of matter. It occurs in nature in both the free and the combined condition.

1. *Free condition.* Free sulfur occurs in many parts of the world, including Sicily, Japan, Spain, Iceland, Mexico, and in different localities in the United States, especially in Louisiana and Texas. The last-named deposits are remarkable for their magnitude and purity. Practically all the sulfur now used in the United States, and some of that used in other countries as well, is obtained from these deposits.

2. *Combined condition.* Large quantities of sulfur also occur in nature in the compounds known as sulfides and sulfates. Some of the most important of these are the following:

SULFIDES		SULFATES	
Galena . . . . .	PbS	Gypsum . . . . .	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
Zinc blende . . . . .	ZnS	Barite . . . . .	$\text{BaSO}_4$
Chalcopyrite . . . . .	$\text{CuFeS}_2$	Celestite . . . . .	$\text{SrSO}_4$
Pyrite . . . . .	$\text{FeS}_2$	Epsom salt . . . . .	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$

Since sulfur is a constituent of protein (p. 249), it is present quite generally in vegetable and animal matter, although only in small quantities. Certain varieties of food, such as the yolks of eggs, contain larger percentages of sulfur.

**Extraction and purification of sulfur.** Native sulfur is mixed with more or less rock and earthy material, amounting in the

case of Sicilian sulfur to nearly 75 per cent of the entire mass. Since the element has a relatively low melting point, its separation from such materials is accomplished by simply heating the mixture. The sulfur melts and drains away from the earthy impurities. The crude sulfur obtained in this way is distilled from an iron retort (Fig. 91, *A*), the exit tube of which

opens into a cooling chamber *B* of brick work. When the sulfur vapor first enters the cold chamber, it condenses in the form of a powder known as *flowers of sulfur*. As the chamber becomes

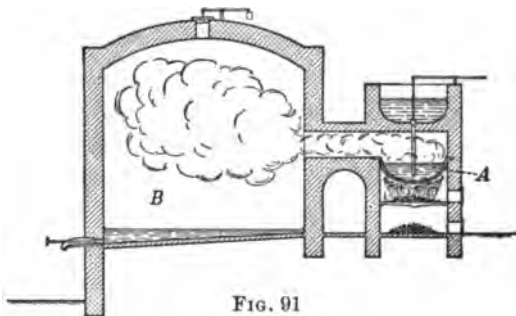


FIG. 91

warmer the vapor condenses to a liquid and is drawn off into cylindrical molds, in which it solidifies, forming the commercial product called *brimstone*.

In Louisiana and Texas wells are sunk into the deposit and superheated water forced down through suitable pipes. The hot water not only melts the sulfur, but, being under pressure, forces it through the tubes to the earth's surface. A single well often produces daily as much as 500 tons of sulfur, which is over 99.5 per cent pure. The production from this source is more than sufficient to meet the needs of the United States.

**Properties.** Sulfur is a pale yellow solid without marked taste or odor. It is insoluble in water. It melts when heated, forming a thin, straw-colored liquid. If the temperature is gradually raised, this liquid turns darker in color and becomes thicker until at about  $235^{\circ}$  it is almost black and is so viscous that a vessel containing it can be inverted without danger of the liquid flowing out. At higher temperatures it becomes mobile again and boils at  $444.6^{\circ}$ , forming a yellowish vapor. On cooling, the same changes take place in reverse order.

Sulfur exists in three allotropic forms, which may be described under two general heads: namely, crystalline sulfur and amorphous sulfur.

**Crystalline sulfur.** Sulfur is a dimorphous element (p. 103), forming crystals which belong either to the rhombic or to the monoclinic system. Both forms are insoluble in water, but are easily soluble in the liquid known as carbon disulfide.

1. *Rhombic sulfur.* Sulfur is sometimes found in nature in crystalline form, and these crystals always belong to the rhombic system. In the laboratory, rhombic crystals may be obtained by allowing a solution of sulfur in carbon disulfide to evaporate spontaneously. While brimstone consists, in the main, of rhombic crystals, one frequently finds, on breaking a stick of it, that the interior portion is made up of crystals having the form of needles, entirely different in shape from the rhombic crystals. These needle-shaped crystals belong to the monoclinic system and are therefore termed monoclinic sulfur.

2. *Monoclinic sulfur.* This form of sulfur is best obtained by slowly cooling melted sulfur. Large crystals may be obtained by melting sulfur in a suitable vessel, allowing a portion of the liquid to solidify and then pouring off the remainder. The solid sulfur adhering to the vessel will be found to consist of distinct monoclinic crystals. These crystals differ from the rhombic not only in shape but in density and melting point, as shown in the following table:

CRYSTAL FORM	DENSITY	MELTING POINT
Rhombic sulfur . . . . .	2.06	112.8°
Monoclinic sulfur . . . . .	1.96	119.25°

**Relation of rhombic to monoclinic sulfur.** Experiments have shown that whenever sulfur crystallizes at ordinary temperature, the rhombic form is always obtained, while at higher temperatures monoclinic crystals are formed. Moreover, the temperature below which sulfur assumes the rhombic form and

above which it is monoclinic is a perfectly definite one, namely  $95.5^{\circ}$ . At this transition point (p. 101) the two forms of crystals remain unchanged when in contact with each other. If heated above  $95.5^{\circ}$ , the rhombic form gradually changes into the monoclinic form; if cooled below  $95.5^{\circ}$ , the reverse change occurs. This change of one form into the other ordinarily takes place very slowly, so that some days may be required before the change is complete. From these facts one can readily understand why the crystals found in nature always have the rhombic form.

**Amorphous sulfur.** We have seen that sulfur melts, when heated, forming a pale yellow, mobile liquid, which at a higher temperature becomes dark and viscous. At intermediate temperatures the liquid obtained consists of varying amounts of the mobile and the viscous liquid in equilibrium with each other. To distinguish the mobile liquid from the thick, viscous liquid, the former is represented by the symbol  $S_{\lambda}$  and the latter by  $S_{\mu}$ . If the liquid sulfur is heated to boiling and poured into cold water, the sudden chilling prevents the crystallization of the viscous liquid, so that an amorphous, dough-like product is obtained.

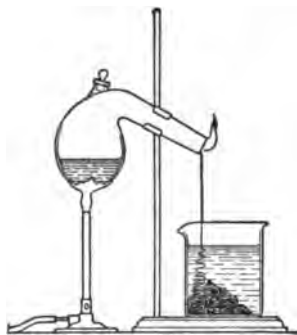


FIG. 92

This form is insoluble in carbon disulfide and is known as *plastic sulfur*. It is largely supercooled liquid sulfur. The formation of plastic sulfur is shown in a striking manner by distilling sulfur from a small, short-necked retort (Fig. 92) and allowing the distillate to run into cold water.

On standing at ordinary temperatures, plastic sulfur changes in part into rhombic crystals. The crystalline portion may then be dissolved in carbon disulfide, leaving an insoluble residue which is amorphous and apparently permanent. The same amorphous form is present in flowers of sulfur, and is left as an insoluble residue when the latter is treated with carbon disulfide.

**Milk of sulfur (sulfur lac).** When an acid is added to aqueous solutions of certain compounds rich in sulfur, a portion of the element is set free and, being insoluble, separates in the form of a white powder, which gives a milky appearance to the entire liquid; hence the name *milk of sulfur*. This form consists chiefly of rhombic crystals. Like all substances formed by precipitation, it is in a fine state of division, and, because of this fact, more readily undergoes chemical changes (p. 33). It is the form commonly used in medicine.

**Chemical conduct.** Sulfur combines directly with many of the elements, metals as well as nonmetals. The compounds formed by its union with some other element are termed *sulfides*, just as the corresponding oxygen compounds are called *oxides*.

1. **Action upon metals.** Most metals, when heated with sulfur, combine directly with it, forming metallic sulfides. In some cases the action is so energetic that the mass becomes incandescent, as has been seen in the case of the reaction of iron with sulfur (p. 10). This property recalls the action of oxygen upon metals, and in general it may be said that the metals which combine readily with oxygen are apt to combine quite readily with sulfur.

2. **Action upon nonmetals.** Under suitable conditions sulfur combines with most of the nonmetals. Thus, with hydrogen it forms the gas hydrogen sulfide ( $\text{H}_2\text{S}$ ); with carbon it forms carbon disulfide ( $\text{CS}_2$ ), a heavy, colorless liquid; with chlorine it forms the liquid chlorides  $\text{S}_2\text{Cl}_2$ ,  $\text{SCl}_2$ , and  $\text{SCl}_4$ . At ordinary temperatures and in the presence of moisture, sulfur reacts slowly with oxygen, forming sulfuric acid; at higher temperatures it burns, forming sulfur dioxide ( $\text{SO}_2$ ), a gaseous compound having the well-known odor of burning sulfur.

3. **Action with oxidizing agents.** When acted upon by oxidizing agents in the presence of water, sulfur is converted into sulfuric acid. Since very accurate methods are known for the determination of sulfuric acid, this reaction is the one generally used in determining the percentage of sulfur present in any substance.

**Uses of sulfur.** Large quantities of sulfur are used in the manufacture of its compounds, such as sulfuric acid and carbon disulfide. It is also used extensively in the manufacture of gunpowder, matches, vulcanized rubber, and insecticides. During the World War large quantities were used in the manufacture of the poison liquid known as "mustard gas."

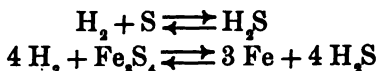
### COMPOUNDS OF SULFUR WITH HYDROGEN

The following compounds of sulfur with hydrogen are known: *hydrogen sulfide* ( $\text{H}_2\text{S}$ ), a foul-smelling gas; *hydrogen persulfide*, a liquid which is probably a mixture of the sulfides  $\text{H}_2\text{S}_2$  and  $\text{H}_2\text{S}_4$ .

**Hydrogen sulfide ( $\text{H}_2\text{S}$ ).** Hydrogen sulfide is often present in the vapors issuing from volcanoes. Dissolved in water, it constitutes the so-called sulfur waters of common occurrence. It is formed when organic matter containing sulfur undergoes decay, and the disagreeable odor attending such changes is often partly due to the presence of this gas.

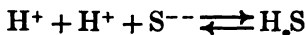
**Preparation.** Hydrogen sulfide may be prepared by the two following general methods:

1. *Synthetic method.* When hydrogen is bubbled through boiling sulfur, a portion of the gas combines directly with the sulfur to form hydrogen sulfide. It is likewise formed when hydrogen is passed over certain sulfides heated to a definite temperature. These reactions are reversible, as is shown in the following equations:

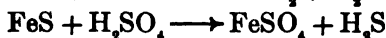
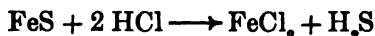


2. *Laboratory method.* Hydrogen sulfide is most conveniently prepared in the laboratory by the action of either dilute sulfuric or hydrochloric acid upon the sulfide of a metal. Iron sulfide ( $\text{FeS}$ ) is usually employed, although when it is used the resulting hydrogen sulfide is not entirely pure. If a greater purity is desired, one may use either sulfide of antimony ( $\text{Sb}_2\text{S}_3$ ),

which is found in nature in a state of great purity, or sodium sulfide, which can be prepared in the laboratory in a pure state. Hydrogen sulfide is very little ionized in solution and is but moderately soluble. Consequently, when an acid is added to a sulfide, the hydrogen ions of the acid and the sulfur ions of the sulfide combine *almost* quantitatively in the equilibrium:



The water present soon becomes saturated with the gas, which then escapes as fast as formed, so that the reaction continues until either the acid or the sulfide is practically all consumed. The following equations serve to show the proportion in which the sulfide and acids interact, as well as the final products formed in each case:



**Apparatus.** To prepare hydrogen sulfide in the laboratory, iron sulfide is placed in a flask *A* (Fig. 98) and dilute acid added drop by drop from the separatory funnel *B*. The hydrogen sulfide formed escapes through the tube *C* and is collected in cylinders, as shown in the figure. The Kipp generator (p. 47) serves as a more convenient form of apparatus for generating the gas. By the evaporation of the liquid left in the generating flask there will be obtained either chloride of iron ( $\text{FeCl}_2$ ) or sulfate of iron ( $\text{FeSO}_4$ ), according to the acid used.

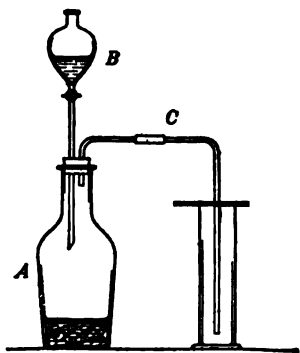


FIG. 98

**Properties.** Hydrogen sulfide is a colorless gas having a mild, disagreeable taste and an offensive odor. It is 1.18 times as heavy as air. The

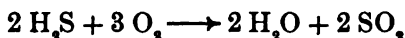
gas may be condensed to a colorless liquid which boils at  $-61.6^\circ$  and solidifies at  $-86^\circ$ . One volume of water at  $15^\circ$  dissolves 3.05 volumes of the gas. When this solution is heated to boiling, the gas is all expelled. In pure form it acts as a violent poison

and, even when diluted largely with air, produces headache, dizziness, and nausea. Fortunately its extremely disagreeable odor gives warning of its presence.

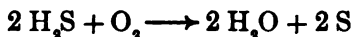
**Chemical conduct.** 1. *Acid properties.* In aqueous solution, hydrogen sulfide is slightly dissociated, giving hydrogen ions. The solution therefore acts as a weak acid and is known as *hydrosulfuric acid*. It possesses the general properties of an acid, turning blue litmus red and neutralizing bases with the formation of sulfides.

2. *Action of heat.* When heated to a moderately high temperature, hydrogen sulfide is decomposed into its elements, the speed of decomposition being marked at 500°.

3. *Action of oxygen.* When a solution of hydrogen sulfide in water (hydrosulfuric acid) is exposed to the air, the hydrogen of the sulfide unites with oxygen to form water, while the sulfur is liberated and settles to the bottom of the liquid. In this way are formed the deposits of the element found about sulfur springs. Hydrogen sulfide is readily inflammable and burns in either oxygen or air, according to the equation



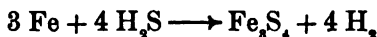
When there is not sufficient oxygen to combine with both the sulfur and the hydrogen, the latter element combines with the oxygen and the sulfur is set free:



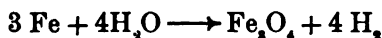
4. *Reducing action.* Because of the hydrogen present, together with the ease with which it is given up in contact with an oxidizing agent, hydrogen sulfide acts as a strong reducing agent. Thus, when it is bubbled through concentrated nitric or sulfuric acid, both of which are strong oxidizing agents, the hydrogen of the sulfide combines with a portion of the oxygen of the acid to form water, the acid being at the same time reduced.

5. *Action upon metals.* The action of hydrogen sulfide upon a number of the metals is very similar to that of water under like conditions, resulting in the displacement of its hydrogen by the

metal. Thus, when it is passed over iron filings heated in a tube, the reaction represented by the following equation takes place :

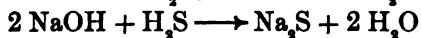
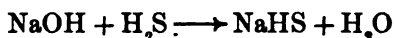


Under similar circumstances steam acts according to the following equation :

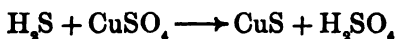


**Salts of hydrosulfuric acid ; sulfides.** The salts of hydrosulfuric acid, termed *sulfides*, form an important class of compounds. They are all solids ; most of them are insoluble in water, while some are insoluble even in acids. As prepared in the laboratory, some of these salts, such as copper sulfide ( $\text{CuS}$ ) and silver sulfide ( $\text{Ag}_2\text{S}$ ), are black ; others, as cadmium sulfide ( $\text{CdS}$ ) and arsenic sulfide ( $\text{As}_2\text{S}_3$ ), are yellow ; while zinc sulfide ( $\text{ZnS}$ ) is white. Many of these sulfides are found in nature (p. 296), some of them constituting the compounds from which the metals are obtained on a commercial scale. They will be frequently mentioned in connection with the metals.

**Preparation of the sulfides.** The soluble sulfides, like those of sodium and potassium, are most readily prepared by treating the respective hydroxides of these metals with hydrosulfuric acid. Both the acid and normal salts may be obtained in this way :



The insoluble sulfides may be prepared by heating the metals with sulfur, although the general and more convenient method of preparing them consists in passing hydrogen sulfide into aqueous solutions of metallic compounds. Thus copper sulfide may be easily prepared by dissolving copper sulfate ( $\text{CuSO}_4$ ) in water and passing hydrogen sulfide into the solution. The copper sulfide, being insoluble, precipitates as fast as formed, and may be removed from the liquid by filtration. The reaction which takes place is expressed in the following equation :



**Precipitation of sulfides.** The preparation of these sulfides as carried out in the laboratory may be illustrated in the following way:

Hydrogen sulfide is generated in a Kipp apparatus *A* (Fig. 94) and is passed successively into bottles *B*, *C*, *D*, *E*, containing, respectively, the aqueous solutions of silver nitrate, cadmium sulfate, zinc acetate, and sodium hydroxide. As the gas bubbles through the solutions there is formed black silver sulfide ( $\text{Ag}_2\text{S}$ ) in *B*, yellow cadmium sulfide ( $\text{CdS}$ ) in

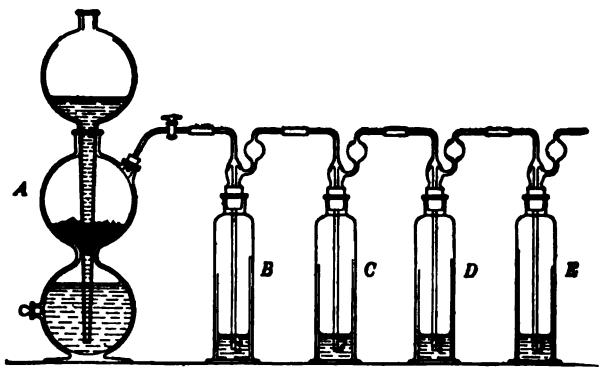


FIG. 94

*C*, white zinc sulfide ( $\text{ZnS}$ ) in *D*. No precipitate is produced in *E*, for although sodium sulfide is formed, it is soluble in water and therefore does not separate.

**The persulfides.** In addition to the ordinary sulfides, which are salts of hydrosulfuric acid, some of the metals form persulfides. As is indicated by the name, these compounds contain a higher percentage of sulfur than the ordinary sulfides. The persulfides of sodium, potassium, and calcium are formed, together with other products, when aqueous solutions of the hydroxides of these metals are heated with sulfur. The exact composition of these persulfides is not known with certainty. They are all unstable, readily decomposing into the ordinary sulfides and free sulfur. Because of this property some of the persulfides are coming into general use as insecticides, the free sulfur being effective for this purpose. Thus the *lime-sulfur spray* that is being used so extensively at present for destroying insects injurious to trees is simply the red solution of calcium persulfide (probably a mixture of  $\text{CaS}_4$  and  $\text{CaS}_5$ ), formed by heating calcium hydroxide with sulfur and water.

When an acid, such as hydrochloric acid, is added to a solution of the persulfide, a portion of the sulfur present is evolved as hydrogen sulfide, and a portion is liberated in the free state (milk of sulfur, p. 300). If, however, in place of adding the acid to the solution of the persulfide, the latter is

added slowly to the acid, a heavy yellow oil separates. This oil is termed hydrogen persulfide and is probably a mixture of the compounds  $\text{H}_2\text{S}_4$  and  $\text{H}_2\text{S}_5$ . This mixture is very unstable, rapidly decomposing into hydrogen sulfide and free sulfur.

### OXIDES AND OXYGEN ACIDS OF SULFUR

With oxygen, sulfur forms the following compounds:

Sulfur dioxide ( $\text{SO}_2$ ), a colorless gas.

Sulfur trioxide ( $\text{SO}_3$ ), a colorless liquid boiling at  $46^\circ$ .

Sulfur sesquioxide ( $\text{S}_2\text{O}_3$ ), a bluish-green crystalline solid.

Sulfur hexoxide ( $\text{S}_2\text{O}_6$ ), a white solid melting at  $50^\circ$ .

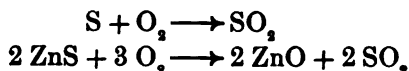
Sulfur heptoxide ( $\text{S}_2\text{O}_7$ ), a viscous liquid.

Of these oxides the first two are by far the most important and best known. They are both acid anhydrides, combining with water to form sulfurous acid and sulfuric acid respectively.

**Sulfur dioxide (sulfurous anhydride) ( $\text{SO}_2$ ).** This is the well-known gas resulting from the combustion of sulfur. It was first obtained in the pure state and recognized as a definite compound by Priestley in 1775. It occurs in nature in the gas issuing from volcanoes and in solution in the waters of some springs.

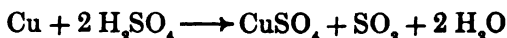
**Preparation.** Sulfur dioxide is prepared by the three following general methods:

1. *By the combustion of sulfur or a metallic sulfide.* In either case the sulfur is converted into sulfur dioxide:



The enormous quantities of sulfur dioxide used in the manufacture of sulfuric acid are prepared by this general method.

2. *By the reduction of sulfuric acid.* When concentrated sulfuric acid is heated with certain metals, such as copper, a part of the acid is reduced to sulfurous acid. The latter compound then decomposes into sulfur dioxide and water, the complete equation being as follows:



A similar reaction takes place when carbon is heated with sulfuric acid:



3. *By the action of acids upon a sulfite.* Sulfites are salts of sulfurous acid ( $H_2SO_3$ ). When an acid, such as hydrochloric acid, is added to a sulfite, sulfurous acid is formed, which decomposes into water and sulfur dioxide. The reactions are expressed in the following equations:

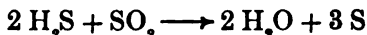


**Explanation of the reaction.** In the action of hydrochloric acid upon sodium sulfite, as expressed in these equations, we have two reversible reactions depending upon each other. It might be expected that the reaction expressed in equation (1) would result in an equilibrium, since none of the substances represented in the equation are insoluble or volatile in the presence of water. The sulfurous acid, however, decomposes as fast as it forms, according to equation (2), the resulting sulfur dioxide escaping in the form of a gas. The reaction continues, therefore, until practically all the sodium sulfite has been decomposed. Since sulfur dioxide is quite soluble in water, it is evident that the reaction should be carried out in the presence of as little water as possible; otherwise a proportionately larger quantity of sulfur dioxide will remain in solution, and the reaction will not reach the same degree of completion.

**Properties.** Sulfur dioxide is a colorless gas and has the peculiar irritating odor so noticeable when sulfur is burned. It is a heavy gas, being 2.2 times as heavy as air. Under standard conditions 1 volume of water dissolves 79.79 volumes of the gas. It is easily liquefied, a freezing mixture of ice and salt being sufficient to effect condensation under atmospheric pressure. The resulting liquid is colorless, boils at  $-8^\circ$ , and freezes to a snowlike solid which melts at  $-76^\circ$ . Liquid sulfur dioxide is a commercial product, being sold in metal cylinders.

The condensation of the sulfur dioxide to a liquid can be accomplished in the following way: Pure sulfur dioxide is generated in *A* (Fig. 95) and conducted into an empty flask *B* surrounded by ice and salt in the ratio 3:1 by weight. The low temperature produced by this mixture is sufficient to condense a portion of the gas to a liquid, which collects in the bottle *B*.

**Chemical conduct.** Sulfur dioxide combines with a number of other substances. Thus, with chlorine it forms the compound known as sulfuryl chloride ( $\text{SO}_2\text{Cl}_2$ ), while with oxygen it forms sulfur trioxide. It also reacts with hydrogen sulfide to form water and free sulfur:



From these statements it will be seen that under some conditions the gas takes up oxygen to form a higher oxide, acting as

a reducing agent; under other conditions it gives up oxygen, acting as an oxidizing agent. It will be remembered that nitric oxide acts in a similar way.

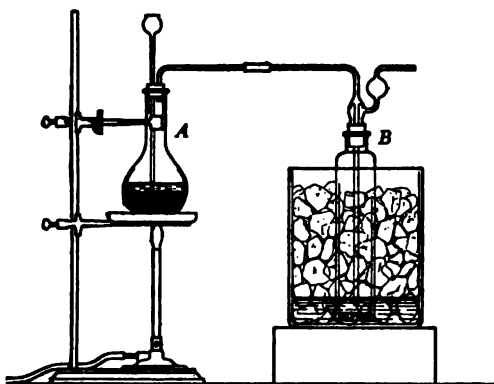


FIG. 95

A very important property of sulfur dioxide is its conduct toward water, with which it unites to form sulfurous acid.

**Sulfurous acid ( $\text{H}_2\text{SO}_3$ ).** When sulfur dioxide is passed into water some of the gas combines with water to form sulfurous acid ( $\text{H}_2\text{SO}_3$ ), while the remainder is held in a state of solution. The sulfurous acid formed is in equilibrium, on the one hand with water and dissolved sulfur dioxide, and on the other hand with the ions  $\text{H}^+$  and  $\text{HSO}_3^-$ , resulting from the ionization of a portion of the acid:

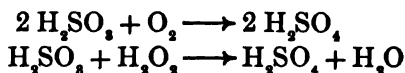


When heated, this liquid acts as if it were simply a solution of sulfur dioxide in water, all the sulfur being evolved as sulfur dioxide. Toward a base, on the other hand, it acts simply as a solution of sulfurous acid (compare with aqua ammonia, p. 255).

Because of its unstable character, sulfurous acid can be obtained only in the form of a dilute solution. This solution has the following properties:

1. *Acid properties.* In aqueous solutions the compound forms the ions  $\text{H}^+$  and  $\text{HSO}_3^-$ . In very dilute solutions some of the latter ions may dissociate further into the ions  $\text{H}^+$  and  $\text{SO}_3^{--}$ . The solution has all the properties of a weak acid.

2. *Reducing properties.* Sulfurous acid is a good reducing agent, taking up oxygen either from the air or from unstable substances containing oxygen, and changing into sulfuric acid, as shown in the following equations:



In this respect it resembles its anhydride  $\text{SO}_2$ , which is also a reducing agent.

Because of this tendency of sulfurous acid to combine with oxygen, a solution of the acid, unless freshly prepared, always contains more or less sulfuric acid. It has been found that the speed of the reaction by which sulfurous acid is changed into sulfuric acid is greatly diminished in the presence of a trace of sugar or glycerin. These latter substances act simply as catalytic agents. While catalyzers are generally employed to increase the speed of a reaction, it will be noted that in this case the sugar and glycerin have just the opposite effect, namely, to diminish the speed of the reaction (p. 280).

3. *Bleaching properties.* Sulfurous acid acts upon many organic dyes, changing them into colorless compounds. It is therefore useful as a bleaching agent, and is used especially to bleach such substances as paper and straw goods, the texture of which would be injured by a more powerful bleaching agent, like chlorine.

*Illustration.* The bleaching properties of sulfurous acid may be shown by bringing a small dish of burning sulfur under a bell jar (Fig. 96) in which has been placed some highly colored flower thoroughly moistened with water. The sulfur dioxide combines with the moisture to form sulfurous acid, which slowly bleaches the flower. The reactions involved in these changes are not thoroughly understood. In some cases the sulfurous

acid apparently combines directly with the coloring matter to form more or less unstable colorless compounds. The gradual decomposition of these compounds into their original constituents would account for the fact that some substances bleached by sulfurous acid gradually regain their original color. In other cases the bleaching properties of the acid seem to be due to its reducing action, whereby oxygen is removed from the water present, while the hydrogen liberated combines with the coloring matter to form colorless compounds.

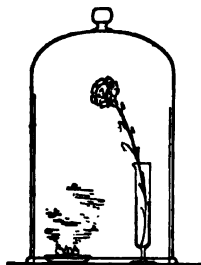
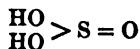


FIG. 96

4. *Antiseptic and preservative properties.* Sulfurous acid destroys many microorganisms and may therefore be used as a disinfectant and also as a preservative, to prevent such changes as decay and fermentation, which are caused by these organisms.

**Structural formula of sulfurous acid.** Both of the following structural formulas have been assigned to the acid, but its chemical reactions are not such as to show which of the two is correct.

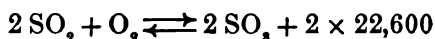


**Uses of sulfurous acid.** Sulfurous acid is used mainly in the preparation of sulfites and as a bleaching agent and preservative. Formerly it was often used for disinfecting rooms after the occurrence of contagious diseases, but it is now largely replaced by formaldehyde (p. 451), which is more effective for the destruction of microorganisms. It is used to a considerable extent in certain foods, such as canned corn, dried fruits, sirups, and wines, serving not only as a preservative but also as a bleaching agent, to remove objectionable colors. Whether or not its use in foods should be permitted is a much-debated question.

**Salts of sulfurous acid; sulfites.** Being dibasic, sulfurous acid forms both acid and normal salts. Thus, with sodium it forms the salts  $\text{NaHSO}_3$  and  $\text{Na}_2\text{SO}_3$ . The sulfites of most of the metals are known, although some of them have not been obtained in pure condition. With the exception of the sulfites of sodium and potassium, the normal sulfites are either insoluble

in water or nearly so, while the acid sulfites are soluble. The normal salts can be prepared either by the action of sulfurous acid upon the hydroxides of the metals or by the general precipitation method used for preparing insoluble compounds. The sulfites are all solid substances and, like sulfurous acid itself, combine readily with oxygen, forming the corresponding sulfates. They are therefore good reducing agents. Because of this property, unless freshly prepared, they are apt to contain more or less of the corresponding sulfates. Calcium acid sulfite is largely used in the manufacture of paper from wood, since it dissolves the objectionable constituent (lignin) of the wood, leaving the pure cellulose which is the material desired for the manufacture of paper.

**Sulfur trioxide (sulfuric anhydride) ( $\text{SO}_3$ ).** When sulfur is burned in oxygen, minute quantities of sulfur trioxide are formed along with the sulfur dioxide. Likewise, when sulfur dioxide and oxygen are heated together, combination takes place, but the speed of the reaction is so slow that only traces of the trioxide result. In the presence of a catalytic agent, however, such as finely divided platinum, the speed is greatly increased, and in this way sulfur trioxide can be obtained in quantities. The reaction is a reversible one, as is shown in the following equation:



The largest yield of sulfur trioxide is obtained when the reaction is carried out at approximately  $400^\circ$ , at which temperature about 98 per cent of the sulfur dioxide combines with oxygen.

**Preparation of sulfur trioxide.** The preparation of the trioxide by this method can be carried out in the laboratory as follows: The platinum used as a catalytic agent is prepared by moistening asbestos fiber in a solution of chloroplatinic acid and igniting it in a flame, whereby the platinum compound is reduced to metallic platinum. The fiber containing the finely divided platinum is placed in a tube of hard glass *A* (Fig. 97), which is then heated to about  $400^\circ$ , while equal volumes of sulfur dioxide and oxygen, previously dried by bubbling them through sulfuric acid (contained in bottles *B* and *C*), are passed into the tube. As this mixture comes in

contact with the catalytic agent, combination takes place, and the resulting sulfur trioxide escapes from the jet at the end of the tube and may be condensed by surrounding the receiving tube *D* with a freezing mixture.

**Properties.** Sulfur trioxide is a colorless liquid which solidifies at about  $15^{\circ}$  and boils at  $46^{\circ}$ . It readily polymerizes (p. 274), especially in the presence of a trace of moisture, forming sulfur hexoxide ( $S_6O_6$ ), a white, crystalline mass somewhat resembling

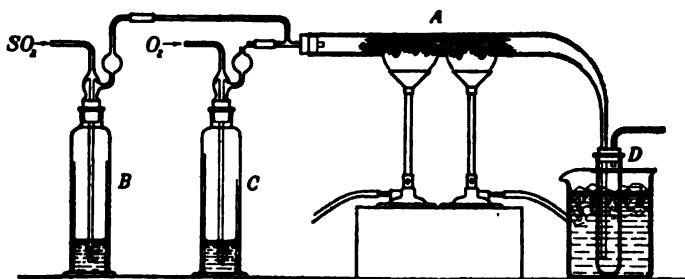


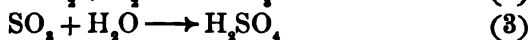
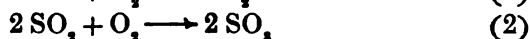
FIG. 97

asbestos in appearance. Toward a substance having a strong affinity for oxygen, sulfur trioxide acts as an oxidizing agent, giving up one third of its oxygen and being reduced to sulfur dioxide. It is characterized especially by its strong affinity for water, with which it combines to form sulfuric acid.

**Sulfuric acid ( $H_2SO_4$ ).** Sulfuric acid has long been known, and was one of the most important reagents employed by the alchemists. It is by far the most largely used of all the acids. Not only is it one of the most common reagents in the laboratory, but enormous quantities of it are consumed in the industries, especially in the manufacture of fertilizers, explosives, and dyes, in the refining of petroleum, and in cleaning scale from iron and steel.

**Manufacture of sulfuric acid.** Two general methods for the manufacture of sulfuric acid are in use at the present time. The newer one of these is known as the contact process, while the older one is called the lead-chamber process.

1. *Contact process.* The reactions taking place in this process are represented by the following equations:



Sulfur dioxide is prepared according to equation (1), by burning sulfur or some sulfide, such as iron pyrite ( $\text{FeS}_2$ ), in air. The resulting sulfur dioxide, together with sufficient air to furnish the necessary oxygen, is conducted through iron tubes filled with some porous material (asbestos or sodium sulfate), through which a suitable catalytic agent, such as iron oxide, is interspersed, the material being kept at about  $400^\circ$ . Under these conditions sulfur trioxide is formed according to equation (2). The resulting sulfur trioxide is then brought into contact with water, with which it unites to form sulfuric acid according to equation (3).

*Details of the contact process.* The only part of the process which is difficult to carry out on a commercial scale is the formation of the sulfur trioxide. It has long been known that sulfur dioxide and oxygen combine when passed over finely divided platinum, but the cost of platinum, together with the poor yield of sulfur trioxide obtained, made the process an impracticable one. A study of the conditions under which the reaction takes place resulted in improvements in the process, until finally, in 1901, the German chemist Knietech succeeded in overcoming the difficulties to such an extent as to make the process a commercial success for the manufacture of the pure, concentrated acid. While platinum is the most effective catalytic agent for the process, it is very expensive, its commercial value at the present time being much greater than that of gold. This has led to the use of other catalytic agents, among which iron oxide appears to be the best.

Some of the more important conditions necessary for making the process a success are the following: (1) The sulfur dioxide must be free from dust particles and other impurities, such as the traces of oxides of arsenic, which are likely to be formed in the combustion of iron pyrite or other sulfides that serve as the source of the dioxide used in the process; otherwise the catalytic agent loses its power. (2) An excess of oxygen over that required in equation (2) must be present. (3) The temperature must be maintained at about  $400^\circ$ . (4) In order that all the sulfur trioxide formed may be completely absorbed, it is passed into sulfuric acid

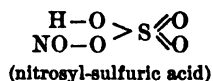
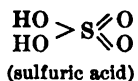
containing from 2 to 3 per cent of water. As the trioxide is absorbed a corresponding amount of water is constantly run in, so that the absorbing solution retains a constant concentration.

2. *Lead-chamber process.* This process receives its name from the fact that the reactions are carried out in large sheet-lead chambers. The following substances enter into the reaction: (1) sulfur dioxide obtained as in the contact process; (2) a mixture of nitric oxide and nitrogen dioxide obtained by heating nitric acid; (3) water in the form of steam; (4) oxygen (air).

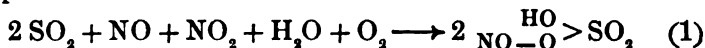
The sulfides of some of the metals, such as zinc and copper, constitute the ores from which these metals are largely obtained. In the extraction of the metals from these ores it is often found most convenient first to convert the sulfides into oxides by heating them in the air. The resulting sulfur dioxide may be utilized in the manufacture of sulfuric acid. It often happens, therefore, that the manufacture of sulfuric acid is carried on in connection with the metallurgy of these metals.

The four substances mentioned above, namely, sulfur dioxide, oxides of nitrogen, steam, and air, are introduced in the proper proportions into large sheet-lead chambers, and under suitable conditions they react to form sulfuric acid. The reactions involved are quite complex, and are not at all thoroughly understood. It is believed, however, that the two following general reactions take place:

1. The substances introduced into the chambers first react to form a derivative of sulfuric acid known as *nitrosyl-sulfuric acid*. The relation of these two compounds to each other may be seen from their structural formulas:

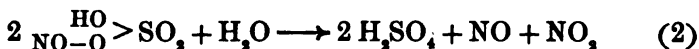


In accordance with these formulas nitrosyl-sulfuric acid differs from sulfuric acid in composition simply by containing the univalent radical NO (known as the *nitrosyl group*) in place of one of the hydrogen atoms of sulfuric acid. Its formation may be represented as follows:



This acid can be obtained in the form of white crystals known as *chamber crystals*.

2. In the commercial manufacture of sulfuric acid, however, such a separation does not occur, because sufficient water is always present to change the nitrosyl acid, as fast as formed, into sulfuric acid:



It will be noted that in this second reaction the same quantities of the oxides of nitrogen are formed as are required for the first reaction. Theoretically, therefore, a small amount of these oxides should suffice to prepare an unlimited amount of sulfuric acid; practically, some of the oxides are lost, and this loss must be replaced. The sulfuric acid collects upon the floor of the chambers in the form of an aqueous solution containing from 62 to 70 per cent of acid. This product is called *chamber acid* and is impure, but for many purposes, such as the manufacture of fertilizers, it needs no further treatment. It can be concentrated by evaporation in open pans made of some material, such as cast iron, lead, or silica, upon which the acid has little or no action. Prepared in this way the ordinary concentrated commercial sulfuric acid usually contains about 5 per cent water as well as small amounts of impurities, especially lead dissolved from the chambers. It also frequently contains traces of arsenic originally present in the sulfides used as the source of the sulfur dioxide. These, however, do not interfere with its use for many purposes. In order to obtain the chemically pure acid, the commercial acid is distilled from vessels made of glass, silica, or porcelain. The distillate consists of approximately 98 per cent acid and 2 per cent water.

**The sulfuric acid plant.** The simpler parts of a plant used in the manufacture of sulfuric acid are illustrated in Fig. 98. Sulfur, or some sulfide as  $\text{FeS}_2$ , is burned in the furnace *A*. The resulting sulfur dioxide, together with the necessary amount of air, passes into the structure *C*, known as the *Glover tower*. In it the oxides of nitrogen are generated, as will be explained below, and these, together with the sulfur dioxide and air, pass

into the chambers *D*, *D*. Water or steam is also introduced into these chambers at suitable points. Here the reactions take place which result in the formation of the sulfuric acid. The nitrogen remaining after the withdrawal of the oxygen from the air which entered the chamber escapes through the structure *E*, known as the *Gay-Lussac tower*. In order to prevent the escape of the nitrogen dioxide regenerated in the reaction, this tower is filled with pieces of coke or porcelain over which trickles concentrated sulfuric acid admitted in fine streams (*F*) at the top. The concentrated acid absorbs the nitrogen dioxide but not the nitric oxide, so

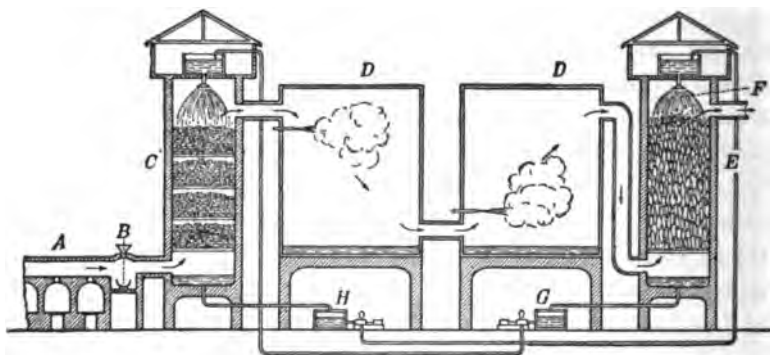


FIG. 98

that the latter escapes along with the nitrogen. The acid which is sprayed into the top of the tower collects in the bottom and is run off into the vessel *G*, from which it is forced into the tank at the top of the Glover tower *C*. Here it is mixed with some dilute sulfuric acid, and the mixture sprayed into the top of the tower, which is partly filled with some acid-resisting rock. As the acid passes down over this material it meets with the hot gases entering from the furnace, whereby the nitrogen dioxide is liberated from the acid, passes over into the chamber *D*, and again enters into the reaction. During the process just described the dilute acid becomes sufficiently concentrated to serve again as an absorbent of nitrogen dioxide. The necessary quantity of it is therefore run into the vessel *H* from the bottom of the tower, and then forced into the tank at the top of *E*. In order to replace the oxides of nitrogen lost in the process, the necessary quantity is added by the action of sulfuric acid upon sodium nitrate in vessel *B*. The sulfuric acid formed collects in the bottom of the chambers and is drawn off from time to time.

**Historical.** The chamber process is a very old one, dating back to the year 1746. For a number of years previous to this date sulfuric acid had been made by burning sulfur mixed with potassium nitrate in large glass

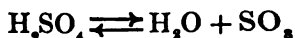
globes. Since these globes were very fragile, and since lead was known to be acted upon to but a very slight extent by the dilute acid, Dr. Roebuck, an Englishman, suggested the substitution of lead-lined chambers for the glass globes. The first plant for the manufacture of the acid by this method was constructed in Birmingham, England, in 1746. The chambers used in the original plant were very small, having a capacity of about 200 cubic feet, while some of those in use at the present time have a capacity as great as 75,000 cubic feet.

**Relative advantages of the contact process and lead-chamber process.** It will be noted that in the contact process it is just as easy to prepare the pure concentrated acid as the dilute acid. In the chamber process, however, the dilute acid is obtained first and can be prepared at a very low cost. The concentration and purification of the dilute acid is, however, an expensive operation. For these reasons the contact process is used only in the manufacture of the concentrated acid.

**Properties.** Pure anhydrous sulfuric acid, more properly termed *hydrogen sulfate*, is a colorless, oily liquid. Because of its oily appearance, together with the fact that it was formerly obtained by distilling the sulfate of iron known as green vitriol, it is often termed *oil of vitriol*. Its density is 1.838 at 15°. When heated to 338° it boils, a portion of the compound decomposing into sulfur trioxide and water in the process. The sulfur trioxide escapes to a greater extent than does the water, until the residual liquid contains 1.67 per cent of water. The resulting mixture then distills with unchanged concentration (p. 179). At a low temperature, hydrogen sulfate forms crystals which melt at 10.5°.

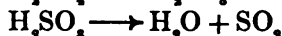
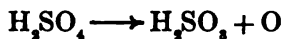
**Chemical conduct of hydrogen sulfate.** The chemical conduct of hydrogen sulfate may be discussed under several topics.

1. *Dissociation by heat.* When heated above 100°, dissociation into water and sulfur trioxide becomes marked, and gradually increases with rising temperature until, at about 450°, it is complete. The reaction is reversible, recombination of the water and sulfur trioxide taking place as the temperature falls:



2. *Oxidizing properties.* Hydrogen sulfate is a strong oxidizing agent, being similar in this respect to hydrogen nitrate (nitric acid). When heated with substances which readily combine

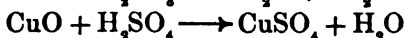
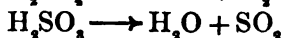
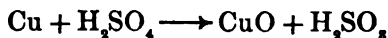
with oxygen, such as carbon, sulfur, and many of the metals, it gives up oxygen to these substances, being itself reduced to sulfurous acid:



It will be recalled that this general reaction serves as one of the methods for preparing sulfur dioxide (p. 306). Because of its strong oxidizing action, hydrogen sulfate is used commercially in the preparation of a number of compounds, such as indigo, and has an advantage in that the sulfur dioxide formed in the process can be changed back into hydrogen sulfate by the contact method, and may thus be utilized repeatedly.

Hydrogen sulfate thus resembles its anhydride  $\text{SO}_2$  in that both are strong oxidizing agents, much as sulfurous acid resembles its anhydride  $\text{SO}_2$  in reducing properties. *It is a general rule that an acid and its anhydride are very similar in oxidizing and reducing properties*, and many examples will be found in subsequent pages.

**3. Action upon metals.** Hydrogen sulfate reacts with most of the metals, especially if heated in contact with them. The action is similar to that of hydrogen nitrate in that the metal is first oxidized, the resulting oxide being then changed into the corresponding salt. Thus the reaction between copper and hydrogen sulfate takes place according to the following equations:



Canceling the formulas of the compounds formed in one reaction and used up in another, — namely,  $\text{H}_2\text{SO}_3$  and  $\text{CuO}$ , — these equations may be combined into the following:



But few of the metals entirely resist the action of hydrogen sulfate. Even platinum and gold, which are very resistant to the action of acids, are perceptibly dissolved when heated with it.

4. *Action upon salts.* The action of hydrogen sulfate upon sodium nitrate (p. 260) is typical of its action upon salts of all acids having a lower boiling point than the hydrogen sulfate itself. This action has been explained in detail in the preceding chapter (p. 286).

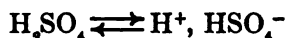
5. *Action upon water.* When hydrogen sulfate is mixed with water, a marked contraction in volume takes place. Moreover, the process is attended by the evolution of a large amount of heat, which may even be sufficient to cause the liquid to boil. Care must therefore be taken, in mixing the sulfate with water, to keep the solution thoroughly stirred during the process, and to pour the sulfate into the water, not the reverse.

When hydrogen sulfate and water are mixed in molecular proportions—namely, 98 parts by weight of the sulfate to 18 of water—and the resulting solution is cooled, the two unite to form the hydrate  $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ . This is a white crystalline substance melting at  $8.5^\circ$ .

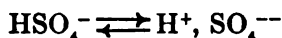
6. *Action upon organic compounds.* Not only does hydrogen sulfate absorb water itself, but it decomposes many compounds containing the elements hydrogen and oxygen. When acted upon by hydrogen sulfate the hydrogen and oxygen present in such compounds unite to form water, which is then absorbed by the sulfate. For example, most organic substances, such as sugar, wood, cotton and woolen fiber, and even flesh (all of which contain hydrogen and oxygen in addition to carbon), are charred by the action of the sulfate, the charring being due to the withdrawal of the hydrogen and oxygen from the compound.

**Chemical conduct of sulfuric acid.** The reactions referred to in the preceding paragraphs are molecular in character rather than ionic, since in solutions of hydrogen sulfate that contain little water it is the molecule  $\text{H}_2\text{SO}_4$  that takes part in the reactions. It is natural to expect, therefore, that a dilute solution of hydrogen sulfate (sulfuric acid) should have different properties from hydrogen sulfate itself, since in such a solution we are dealing with ions rather than molecules.

When water is added to hydrogen sulfate, ionization at first takes place as follows:

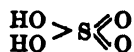


Upon the further addition of water more molecules are ionized, while the  $\text{HSO}_4^-$  ions formed in the concentrated solutions are changed as follows:



In concentrated solutions the extent of ionization is limited; thus, in a solution containing 5 per cent of water, less than 1 per cent of the molecules are ionized, while in a normal solution (49 g. of  $\text{H}_2\text{SO}_4$  in 1 l. of solution) only about half of the molecules are ionized. Concentrated solutions of sulfuric acid react, therefore, much like hydrogen sulfate itself. Dilute solutions, on the other hand, act like typical acids.

**Structural formula of hydrogen sulfate.** The chemical conduct of hydrogen sulfate is best explained upon the assumption that the molecule contains two hydroxyl groups, and that these groups, as well as the remaining oxygen atoms, are directly bound to the sulfur, as indicated in the following formula, in which the sulfur is hexavalent:



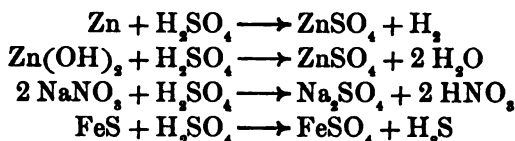
This formula is often abbreviated to the form  $\text{SO}_4(\text{OH})_2$ .

**Salts of sulfuric acid; sulfates.** The sulfates constitute a very important class of compounds, and many of them have extensive commercial uses. The normal salts are all solids and, with the exception of those of barium, strontium, and lead, are soluble in water. Two others, namely, calcium sulfate and silver sulfate, are only slightly soluble. The hydrates of many of the sulfates are more frequently used than the anhydrous salts. Some of the more important of these compounds are included in the table on the following page.

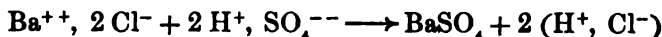
# SULFUR; SELENIUM; TELLURIUM; HYDROLYSIS 321

FORMULA	CHEMICAL NAME	COMMON NAME
$\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$	Hydrate of sodium sulfate	Glauber's salt
$\text{MgSO}_4 \cdot 7 \text{H}_2\text{O}$	Hydrate of magnesium sulfate	Epsom salt
$\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$	Hydrate of calcium sulfate	Gypsum
$\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$	Hydrate of copper sulfate	Blue vitriol
$\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$	Hydrate of iron sulfate	Green vitriol or copperas
$\text{ZnSO}_4 \cdot 7 \text{H}_2\text{O}$	Hydrate of zinc sulfate	White vitriol
$\text{BaSO}_4$	Barium sulfate	Barite or heavy spar

The sulfates can be prepared by the action of sulfuric acid upon the metals, their oxides and hydroxides, and many of their salts, as illustrated by the following equations:



The insoluble sulfates may be prepared by the general method used in preparing insoluble compounds. Thus barium chloride ( $\text{BaCl}_2$ ) and sulfuric acid in aqueous solutions react as indicated in the equation:



The resulting barium sulfate separates in the form of a white solid. Since only soluble sulfates and sulfuric acid yield the ion  $\text{SO}_4^{--}$  in solution, this reaction serves as a delicate test for these compounds.

**Other oxygen acids of sulfur.** In addition to sulfurous and sulfuric acids a number of other oxygen acids of sulfur are known, either in the free state or in the form of their salts. The formulas and names of these are as follows:

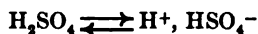
Thiosulfuric acid . . . . .	$\text{H}_2\text{S}_2\text{O}_3$	Dithionic acid . . . . .	$\text{H}_2\text{S}_2\text{O}_6$
Hyposulfurous acid . . . . .	$\text{H}_2\text{S}_2\text{O}_4$	Trithionic acid . . . . .	$\text{H}_2\text{S}_3\text{O}_6$
Pyrosulfuric acid . . . . .	$\text{H}_2\text{S}_4\text{O}_7$	Tetrathionic acid . . . . .	$\text{H}_2\text{S}_4\text{O}_8$
Persulfuric acid . . . . .	$\text{H}_2\text{S}_8\text{O}_{22}$	Pentathionic acid . . . . .	$\text{H}_2\text{S}_5\text{O}_{15}$

The thionic acids derive their names from a Greek word meaning "sulfur." With the exception of pyrosulfuric acid, the acids

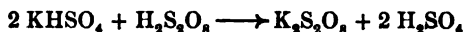
are so unstable that they have been obtained only in dilute aqueous solution or in the form of salts. A brief discussion of pyrosulfuric and persulfuric acid follows. The important salts of the other acids will be discussed in their appropriate places in connection with the metals.

**Pyrosulfuric acid ( $\text{H}_2\text{S}_2\text{O}_7$ ).** Sulfur trioxide dissolves in sulfuric acid in all proportions, forming *fuming sulfuric acid*, often called *oleum*. This acid is of importance especially in the manufacture of dyes. If the sulfur trioxide and sulfuric acid are mixed in molecular proportions, the two combine to form a solid crystalline compound,  $\text{H}_2\text{S}_2\text{O}_7$ , known as *pyrosulfuric acid*.

**Persulfuric acid ( $\text{H}_2\text{S}_2\text{O}_8$ ).** It will be recalled that in concentrated solutions of sulfuric acid there exists the equilibrium expressed in the following equation:

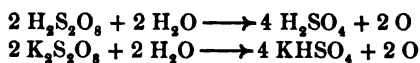


When such solutions are electrolyzed, hydrogen is evolved at the cathode. At the anode the ions  $\text{HSO}_4^-$  are discharged, and under certain conditions the resulting radicals combine with each other to form the compound  $(\text{HSO}_4)_2$ , or  $\text{H}_2\text{S}_2\text{O}_8$ , which remains dissolved in the liquid about the anode. This compound is known as *persulfuric acid*. While the acid is unstable and exists only in dilute solution, its salts can be obtained in pure condition. They are prepared by the electrolysis of concentrated solutions of the corresponding acid sulfates. For example, a concentrated solution of potassium hydrogen sulfate, upon electrolysis, yields persulfuric acid at the anode, just as does the electrolysis of sulfuric acid itself. The acid, however, as fast as formed, reacts with the potassium hydrogen sulfate present in the solution to form potassium persulfate:



The potassium salt, being sparingly soluble, crystallizes as a white solid.

Persulfuric acid, as well as its salts, is a strong oxidizing agent. In the presence of a reducing agent, aqueous solutions of the acid and its salts decompose as follows, the oxygen combining with the reducing agent:



Some of the persulfates are used as oxidizing agents for special purposes.

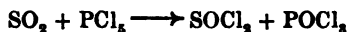
**Compounds containing sulfur and chlorine.** The following compounds containing sulfur and chlorine are known:

1. *Sulfur monochloride* ( $S_2Cl_2$ ). This compound was formerly thought to have the formula  $SCl$ , hence the name *monochloride*. It is formed when chlorine is passed over heated sulfur, and is a yellow, oily liquid boiling at  $138^\circ$  and having an extremely disagreeable odor. It is a good solvent for sulfur, and this solution is used in vulcanizing rubber. During the World War large amounts were used in the manufacture of the poison liquid known as "mustard gas."

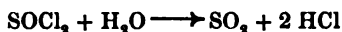
2. *Sulfur dichloride* ( $SCl_2$ ). When sulfur monochloride is saturated with chlorine at from  $6^\circ$  to  $10^\circ$ , the dichloride is obtained. It is a reddish-brown liquid which boils at  $64^\circ$ .

3. *Sulfur tetrachloride* ( $SCl_4$ ). At low temperatures sulfur dichloride combines with additional chlorine to form a reddish-brown liquid which has the composition  $SCl_4$ . This compound is stable only at temperatures below  $-20^\circ$ . As the temperature rises it gradually decomposes into sulfur dichloride and free chlorine.

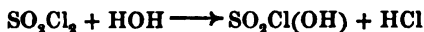
4. *Thionyl chloride* ( $SOCl_2$ ). This compound is obtained, along with phosphorus oxychloride ( $POCl_3$ ), by the action of sulfur dioxide upon phosphorus pentachloride ( $PCl_5$ ):



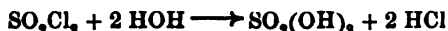
Thionyl chloride is a colorless liquid boiling at  $78^\circ$ . With water it decomposes as indicated in the following equation:



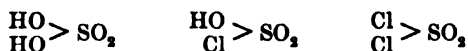
5. *Sulfuryl chloride* ( $SO_2Cl_2$ ). Under proper conditions sulfur dioxide and chlorine combine directly to form sulfuryl chloride, a compound having the formula  $SO_2Cl_2$ . The reaction may be greatly hastened by using camphor as a catalytic agent. Sulfuryl chloride is a colorless liquid and has a pungent odor. It has a density of 1.67 and boils at  $69^\circ$ . In the presence of a relatively small quantity of water one of the chlorine atoms is displaced by a hydroxyl group, forming the compound  $SO_2Cl(OH)$ , known as chlorosulfonic acid:



With an excess of water both atoms of chlorine are displaced by hydroxyl groups, forming sulfuric acid:



The structural relations of sulfuric acid, chlorosulfonic acid, and sulfuryl chloride to each other are shown in the following formulas:



**The valence of sulfur.** The valence of sulfur varies in its different compounds. It is reasonably certain that it is bivalent in hydrogen sulfide ( $\text{H}-\text{S}-\text{H}$ ) and hexavalent in hydrogen sulfate. In sulfurous acid it is uncertain whether it is quadrivalent or hexavalent (see p. 310). If the oxygen atoms in sulfur dioxide and sulfur trioxide are all directly bound to sulfur, then the element in these compounds is quadrivalent and hexavalent respectively. Nothing is known of the valence of sulfur in its more complex acids and salts, since their structure has not been determined.

#### SELENIUM AND TELLURIUM

The elements *selenium* and *tellurium* may appropriately be considered in connection with sulfur, because of their intimate relation to this element. Selenium resembles sulfur in many of its properties, as well as in its chemical conduct. While tellurium does not show this marked similarity, nevertheless its compounds are closely related in composition to those of sulfur.

Tellurium was discovered by Reichenstein and Klaproth in the latter part of the eighteenth century. The latter investigator gave to the element the name it now bears, the word meaning "the earth." A few years later (1817) Berzelius isolated a new element, which he named selenium, from a Greek word meaning "the moon." Both of these elements occur in nature in the free as well as in the combined condition, but only in comparatively small quantities, being far less abundant than sulfur.

**Selenium.** This element is frequently found in small quantities in natural sulfur. Combined with metals it also occurs along with some of the sulfides, especially pyrite ( $\text{FeS}_2$ ). When sulfur or a sulfide, containing selenium is used in the manufacture of sulfuric acid, some free selenium is always found in the flue dust, as well as in the slime collecting in the bottom of

the lead chambers, and it was from this material that Berzelius first isolated the element.

**Properties.** Selenium resembles sulfur in that it occurs in a number of different forms, although the relation of these to each other has not been so well determined as in the case of sulfur. The most important of these forms are the following: (1) a red amorphous solid, slightly soluble in carbon disulfide; (2) a red crystalline solid, likewise slightly soluble in carbon disulfide; (3) a gray metallic crystalline solid, insoluble in carbon disulfide. In this last form selenium is a conductor of electricity, and it is an interesting fact that its conductivity increases with the intensity of the light to which the selenium is subjected. When heated in the presence of air it forms selenium dioxide ( $\text{SeO}_2$ ).

Considerable selenium is recovered each year in the United States as a by-product in the refining of copper, and more could be produced if there were a demand for it. At present about the only use for it is as the coloring agent in the manufacture of red glass. An effort is being made to find further uses for the element.

**Compounds of selenium.** In general it may be stated that its compounds resemble those of sulfur, in composition as well as in general properties. The most important of these compounds are as follows: (1) hydrogen selenide ( $\text{H}_2\text{Se}$ ), a gas of unbearable odor; (2) selenium dioxide ( $\text{SeO}_2$ ), a white crystalline solid formed by burning selenium in air; (3) hydrogen selenite ( $\text{H}_2\text{SeO}_3$ ), an unstable white crystalline solid formed by the combination of selenium dioxide and water; (4) hydrogen selenate ( $\text{H}_2\text{SeO}_4$ ), a solid melting at  $58^\circ$ , its aqueous solutions (selenic acid) resembling sulfuric acid in properties and chemical conduct; (5) salts derived from the acids  $\text{H}_2\text{Se}$ ,  $\text{H}_2\text{SeO}_3$ , and  $\text{H}_2\text{SeO}_4$ , in a general way resembling those of the corresponding sulfur compounds. Lenher discovered that selenium oxychloride, a liquid of the composition indicated by formula  $\text{SeOCl}_2$ , is an excellent solvent for a wide range of materials.

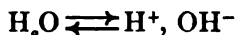
**Tellurium.** While small quantities of tellurium occur in nature in the free state, it is much more frequently found

combined with metals, especially gold, silver, lead, and bismuth, forming compounds known as *tellurides*. In separating these metals from their ores considerable quantities of tellurium are often obtained, although no commercial use has yet been found for it. The pure element resembles the metals in appearance. It has a silvery luster and, like the metals, it conducts electricity. It has a density of 6.2 and melts at 452°. When heated in the air, it burns, forming tellurium dioxide ( $\text{TeO}_2$ ).

**Compounds of tellurium.** Some of the more important compounds of tellurium are the following: (1) hydrogen telluride ( $\text{H}_2\text{Te}$ ), an unstable gas of disagreeable odor, which resembles hydrogen sulfide in its properties; (2) tellurium dioxide ( $\text{TeO}_2$ ), a white solid formed by the combustion of tellurium in oxygen or air; (3) tellurium trioxide ( $\text{TeO}_3$ ), an orange-yellow solid formed by the careful heating of hydrogen tellurate; (4) hydrogen tellurite ( $\text{H}_2\text{TeO}_3$ ), a white powder formed by the oxidation of tellurium with nitric acid; (5) hydrogen tellurate ( $\text{H}_2\text{TeO}_4$ ), a solid formed by the action of strong oxidizing agents upon tellurium, its aqueous solution (telluric acid) having very weak acid properties. Salts of the different acids of tellurium are also known.

#### HYDROLYSIS

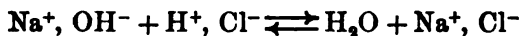
While for most purposes we make no important error in assuming that water is an un-ionized compound, there are many reactions that keep reminding us that the purest of water has a slight but measurable degree of ionization. The gram-molar concentration of the  $\text{H}^+$  and the  $\text{OH}^-$  ions in pure water is  $1.1 \times 10^{-7}$ , or about 0.1 mg. of H and 1.7 mg. of OH per ton. While this is very small expressed in *weight*, it still means millions of each kind of ions per cubic centimeter, and also that *these are constantly maintained* through the equilibrium



Because of this distinct (though slight) ionization water takes part in many reactions of the type we have been calling double

decomposition, all of which depend upon the presence of free ions in solution. *A reaction of double decomposition that depends upon the presence of the ions formed from water is called hydrolysis.*

**Hydrolysis and neutralization.** Since water undergoes this slight but very constant ionization, it is clear that the process of neutralization which depends upon the union of hydrogen ions with hydroxyl ions is never entirely complete but ends in a state of equilibrium:



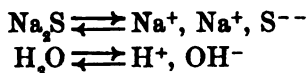
For if water is even slightly ionized, the reverse reaction will be set up to a slight extent, and by the definition we have just formulated, this will be a slight *hydrolysis* of the salt formed in neutralization. It will thus be seen that hydrolysis of a salt is just the reverse of neutralization.

Under certain conditions salts show a very marked degree of hydrolysis in solution, and the salts of the various acids of sulfur illustrate the principles involved very admirably. We may therefore with profit study the subject of hydrolysis of salts at this point.

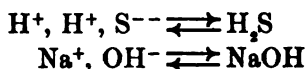
**Hydrolysis of salts.** The hydrolyzing action of water with salts presents four distinct cases, which will be considered in order.

1. *Hydrolysis of a salt derived from a strong base and a weak acid.*

All salts derived from a strong base and a weak acid have an *alkaline* reaction in solution, and consequently there must be an excess of hydroxyl ions in the solution. Sodium sulfide will serve as an example, being derived from sodium hydroxide and hydrosulfuric acid. When this salt is added to water the reactions expressed in the following equations take place:



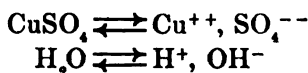
But each positive ion in the solution must be in equilibrium with each negative ion, so that there will be two other equilibria:



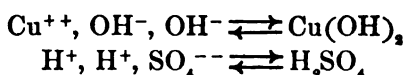
In the first of these the product formed,  $\text{H}_2\text{S}$ , is a *very weak acid* and is consequently little ionized, so that equilibrium is not reached until almost all the hydrogen ions have entered into combination. In the second equilibrium the product formed,  $\text{NaOH}$ , is a *strong base* and is largely ionized. As a result of these differences more hydrogen ions are withdrawn in the first equilibrium than hydroxyl ions in the second, and the solution *acquires basic properties from the excess of hydroxyl ions*.

2. *Hydrolysis of a salt derived from a strong acid and a weak base.*

Salts belonging to this class yield *acid* solutions, and consequently these solutions must have an excess of hydrogen ions. Copper sulfate will serve as an example. When this salt is dissolved in water the equilibria represented in the following equations result:



But in addition to these there must be the further equilibria expressed in the following equations:



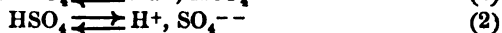
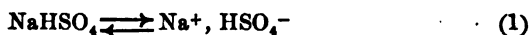
In the first of these the product formed,  $\text{Cu}(\text{OH})_2$ , is a *very weak base* and is therefore little ionized, so that at equilibrium most of the hydroxyl ions are withdrawn from the solution. With sulfuric acid formed in the second equilibrium the case is quite different, since it is a *strong acid* and is largely ionized. As a result of these differences more hydroxyl ions are withdrawn than hydrogen ions, and consequently the *solution acquires acid properties*.

3. *Hydrolysis of a salt derived from a strong base and a strong acid.* All such salts yield neutral solutions. It is evident from the above discussions that when salts of this class are dissolved in water neither the hydrogen nor the hydroxyl ions are withdrawn in appreciable amounts; hence their solutions are neutral.

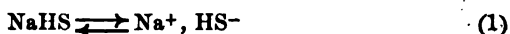
4. *Hydrolysis of a salt derived from a weak base and a weak acid.*

Such salts are more or less completely decomposed in the presence of water.

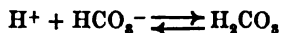
The action of water upon acid salts. The acid salts of strong acids readily ionize in aqueous solutions yielding hydrogen ions. Thus sodium hydrogen sulfate ionizes as follows:



In dilute solutions both of the reactions expressed in (1) and (2) are practically complete. Such solutions, therefore, have an acid reaction due to the hydrogen ions. The case is different, however, with acid salts of weak acids, since the hydrogen present in such salts is not ionized to any appreciable extent when the salts are dissolved in water. Sodium hydrogen sulfide, for example, ionizes as follows:



The reaction expressed in (2), however, takes place only to a very slight extent. A solution like this will therefore contain such a comparatively small number of hydrogen ions that it will have either a neutral or, at most, only a slightly acid reaction. Indeed, in the case of acid salts derived from a strong base and a very weak acid, hydrolysis may take place to such an extent that their solutions react basic. For example, sodium hydrogen carbonate ( $\text{NaHCO}_3$ ), an acid salt of carbonic acid ( $\text{H}_2\text{CO}_3$ ), dissolves in water, forming the ions  $\text{Na}^+$  and  $\text{HCO}_3^-$ . Since carbonic acid is a very weak acid scarcely ionizing at all in solution, it will be formed by the union of ions  $\text{HCO}_3^-$  with the hydrogen ions of the water:



This withdrawal of the hydrogen ions from the water results in the accumulation of the accompanying hydroxyl ions to such an extent that the solution becomes basic in reaction.

## QUESTIONS

1. Would concentrated sulfuric acid serve as a suitable drying agent for hydrogen sulfide?

2. (a) Write the equations for the preparation of the following acids from their salts: hydrochloric, nitric, nitrous, hydrosulfuric, sulfurous. (b) Point out the similarity in the methods. (c) Can sulfuric acid be prepared by this same general method?

3. The use of sulfuric acid in the preparation of other acids is based upon what general property?
4. Zinc dissolves in both concentrated and dilute solutions of sulfuric acid. Write the equations for the reactions in both cases and contrast the products formed.
5. Suggest two methods for liberating the sulfur from hydrogen sulfide.
6. Suggest a reason for the large evolution of heat when water is added to hydrogen sulfate.
7. (a) What components are present in a concentrated solution of sulfuric acid? (b) in a dilute solution of the acid?
8. Suppose you wished to build a plant for the manufacture of sulfuric acid. What factors would you take into consideration in selecting the location of your proposed plant?
9. What impurities are likely to be present in commercial sulfuric acid?
10. Would you expect a solution of sodium acetate to have any action on litmus? (See p. 242 for strength of acetic acid.)

### PROBLEMS

1. Much of the sulfur dioxide used in the manufacture of sulfuric acid is prepared by the combustion of pyrite,  $\text{FeS}_2$ . What weight of this sulfide would be required in a sulfuric acid plant that has a daily output of 100 tons of acid containing 65 per cent of  $\text{H}_2\text{SO}_4$ , assuming that 10 per cent of the sulfur in the pyrite is lost in the operation.
2. Upon analysis a compound was found to have the following composition: sulfur, 39.07 per cent; oxygen, 58.49 per cent; hydrogen, 2.44 per cent. Calculate its formula (p. 114).
3. Calculate the percentage composition of sulfuric acid.
4. Suppose you had as available raw materials sulfur and sodium chloride and wished to prepare 100 kg. of sodium sulfite daily. (a) What weights of the raw materials would be required? (b) What by-products would be formed in the process selected?
5. 25 cc. of a normal solution of sodium hydroxide was required to neutralize the acid present in 10 g. of a sample of sulfuric acid. Calculate the percentage of acid present in the solution.

## CHAPTER XX

### THE PERIODIC LAW; THE STRUCTURE OF ATOMS

#### THE PERIODIC LAW

**Introduction.** Almost as soon as the atomic theory was proposed it was felt that all the various kinds of atoms could not be utterly unlike, but that there should be groups or families of elements whose atoms would have somewhat similar properties. We have seen that the inactive gases of the atmosphere constitute one such group, and sulfur, selenium, and tellurium another. As the number of known elements increased through new discoveries an increasing interest was felt in the problem of classification of the elements into natural groups, and a great many plans were suggested for securing such an arrangement.

**Classification based on chemical conduct.** As soon as a reasonably clear distinction had been made between acids and bases the elements were divided into two great classes, according to whether their oxides formed acids or bases on hydration, and they were called respectively *acid-forming* and *base-forming* elements. Even such a broad classification was not free from difficulties, since many elements form several oxides, and it frequently happens, as with manganese and chromium, that some oxides form acids, while others of the same element form bases.

**Metals, nonmetals, and metalloids.** Those elements which usually form bases have in general the properties which we ordinarily associate with the term *metal*. They are rather heavy, have a bright, shining surface, or a luster, are ductile and malleable, and are good conductors of heat and electricity. The acid-forming elements have the opposite properties, being of small density, of little or no luster, brittle, and of small conducting capacity.

There are, however, numerous cases in which these distinctive marks fail. Thus sodium and potassium are very light, though undoubtedly metals; silicon is rather heavy and has a high luster, though a nonmetal. Gradually the terms *metal* and *nonmetal* came to be used as practically synonymous with *base-forming element* and *acid-forming element*. An intermediate group of elements which possessed in some degree the physical properties of metals and the chemical conduct of nonmetals came to be known as *metalloids*. Examples of this class are arsenic, antimony, and tellurium.

**Classifications based on atomic weights.** Many attempts have been made to base a classification of the elements upon some relation between their atomic weights. These are the most characteristic and fundamental property of the elements, and it is here, if anywhere, that we should expect to find a basis for a natural grouping.

**The triads of Döbereiner.** In 1829 Döbereiner showed that many of the elements may be arranged in groups of three closely similar ones, in which the atomic weight and the general properties of the one are almost an exact arithmetical mean between the other two. Thus we have

Ca . . 40.07	Mg . . 24.32	Cl . . 35.46
Sr . . 87.63 (88.72)	Zn . . 65.37 (68.36)	Br . . 79.92 (81.19)
Ba . . 137.37	Cd . . 112.40	I . . 126.92

The numbers in the parentheses indicate the real mean between the weights. Many other relations of the same general kind were discovered later, so that chemists came to feel that in some way the magnitude of the atomic weight of an element really determines its properties.

**Methods of finding relationships.** There are two general methods available in solving a problem such as the one we have before us. One is to become as familiar as possible with all the peculiarities of each individual, and merely through familiarity come to recognize types or family resemblances. This is the way we ordinarily classify our personal friends, and it was the method followed by most of the earlier chemists. The difficulty with this method is that too much depends upon mere opinion.

A much more scientific way is to select what seems to be the most fundamental property common to all the individuals, and arrange them in the order in which this property increases, observing how other properties fall in with this order.

**Classification of Mendeléeff and Meyer.** In 1869 two distinguished chemists, the Russian Mendeléeff and the German Lothar Meyer, quite independently of each other, followed the method just described and discovered a relation between the atomic weights of the elements and their other physical properties and their chemical conduct that has come to be known as the *periodic law*. An exact statement of the law will be understood better after the method of arrangement has been explained.

**Plan of arrangement.** The atomic weight was selected as the most fundamental property of atoms, and the elements were arranged with reference to this. Omitting hydrogen, the first eight elements are:

He (4.0) Li (6.94) Be (9.1) B (10.9) C (12.006) N (14.008) O (16.0) F (19.0)

These elements all differ markedly from each other, but the ninth element, neon, is very similar to helium. It is placed just below the latter, and a new row follows:

Ne (20.2) Na (23.0) Mg (24.32) Al (27.1) Si (28.3) P (31.04) S (32.06) Cl (35.46)

The next element, argon, again resembles helium and neon, and begins a third row:

Ar (39.9) K (39.1) Ca (40.07) Sc (45.1) Ti (48.1) V (51.0) Cr (52.0) Mn (54.93)

An inspection of the elements in the eight vertical columns brings to light a remarkable fact. Not only are helium, neon, and argon very similar, but a more or less pronounced resemblance is found between the several elements in each of the columns. Thus lithium, sodium, and potassium are very similar, as are glucinum, magnesium, and calcium.

The three elements following manganese — namely, iron, cobalt, and nickel — resemble each other very closely, and if arranged as the first three elements in a fourth row, they would interrupt the regularities so far exhibited. They are set aside

in a ninth column, and the other elements are arranged as before. The complete table is shown on page 335. A vertical row is called a *group*, a horizontal row a *series*. It will be noticed that two other sets of three elements are placed in the ninth column, and that some blank spaces appear in the table, representing elements as yet undiscovered.

**The relation of properties to atomic weights.** There is evidently an intimate relationship between the properties of an element and its atomic weight. Helium, at the beginning of the first row, has no chemical activity at all. Lithium is a metallic element of very strong base-forming character and a valence of 1. Glucinum is also a metal, but with less strongly marked base-forming character and a valence of 2. Boron is a metalloid, is much more acid-forming than basic in character, and has a valence of 3. In carbon, with a valence of 4, all basic properties have disappeared, and it is an acid-forming element exclusively. The succeeding elements, nitrogen, oxygen, and fluorine, are increasingly acid-forming, while the valence increases to 7. A somewhat similar change may be noticed in many of the physical properties of the elements, such as their conductivity toward heat and electricity, their densities, and their melting points. These properties usually vary with some regularity as we pass from one end of a series to the other; or, in mathematical language, the properties are continuous functions of the atomic weights.

**The periodic law.** If helium were the element of smallest atomic weight and fluorine that of the greatest, so that in passing from helium to fluorine we had passed all the elements in review, we could make the general statement that the properties of the elements vary directly with their atomic weights. But fluorine has a small atomic weight, and neon, which follows it, repeats the properties of helium, starting a new series, or period. If we omit the elements in the ninth column, we see that each ninth element starts a new period, and we reach a *statement of the periodic law*, which is: *The properties of elements are periodic functions of their atomic weights.*

THE PERIODIC ARRANGEMENT OF THE ELEMENTS

Type of hydrides and chlorides . . . . .	RH	RH <sub>2</sub>	RH <sub>3</sub>	RH <sub>4</sub>	RH <sub>5</sub>	RH <sub>6</sub>	RH <sub>7</sub>	RH <sub>8</sub>	RO <sub>2</sub>
Type of oxides . . . . .	R <sub>2</sub> O	RO	RO <sub>2</sub>	RO <sub>3</sub>	RO <sub>4</sub>	RO <sub>5</sub>	RO <sub>6</sub>	RO <sub>7</sub>	RO <sub>8</sub>
SERIES	GROUP I	GROUP II	GROUP III	GROUP IV	GROUP V	GROUP VI	GROUP VII	GROUP VIII	
1	Li = 6.94 (3)	Ga = 9.1 (4)	B = 10.9 (5)	C = 12.005 (6)	N = 14.006 (7)	O = 16.0 (8)	F = 19.0 (9)		
2	Na = 23.0 (11)	Mg = 24.32 (12)	Al = 27.1 (13)	Si = 28.3 (14)	P = 31.04 (15)	S = 32.06 (16)	Cl = 35.46 (17)		
	A	A	A	A	A	A	A		
3	K = 39.1 (19)	Ca = 40.07 (20)	Sc = 45.1 (21)	Ti = 48.1 (22)	V = 51.0 (23)	Cr = 52.0 (24)	Mn = 54.93 (25)	Fe = 55.84 (26) Co = 58.97 (27) Ni = 58.68 (28)	
4	Cu = 63.57 (29)	Zn = 65.37 (30)	Ga = 70.1 (31)	Ge = 72.5 (32)	As = 74.96 (33)	Se = 79.2 (34)	Br = 79.92 (35)		
5	Rb = 85.45 (37)	Sr = 87.63 (38)	Y = 89.33 (39)	Zr = 90.6 (40)	Cb = 93.1 (41)	Mo = 96.0 (42)		Ru = 101.7 (44) Rh = 102.9 (45) Pd = 106.7 (46)	
6	Ag = 107.88 (47)	Cd = 112.4 (48)	In = 114.8 (49)	Sn = 118.7 (50)	Sb = 120.2 (51)	Te = 127.5 (52)	I = 126.92 (53)		
7	Cs = 132.81 (55)	Ba = 137.37 (56)	La = 139.0 <sup>1</sup> (57)	Ce = 140.26 (58)	Ta = 181.5 (73)	W = 184.0 (74)		Os = 190.9 (76) Ir = 193.1 (77) Pt = 195.2 (78)	
8	Au = 197.2 (79)	Hg = 200.6 (80)	Tl = 204.0 (81)	Pb = 207.2 (82)	Bi = 208.0 (83)	Po = ? (84)			
9	Nt = 223.4 (86)	Ra = 226.0 (88)	Ac = ? (89)	Th = 232.15 (90)	U <sub>x</sub> = ? (91)	U = 238.2 (92)			

<sup>1</sup> Along with La, belong a group of elements called the rare earth metals. They all closely resemble La and have atomic numbers 57-72, sixteen in all. All but one of these are known. One of these, cerium, has some properties that warrant placing it in Group IV.

**The atmospheric elements.** Until a few years ago the elements in the column marked 0 were unknown. When they were discovered they were seen to constitute a group by themselves, falling between the very strong acid-forming elements and the equally strong base-forming ones. It was therefore very interesting that they should have no chemical activity, but should serve as a sort of bridge between the elements. Rather than renumber the old columns, thus creating some confusion, the new one was added as column 0, this designation having a certain fitness, since the elements in it have no chemical activity.

**The atomic number.** Under the symbol of each element is placed a numeral called the *atomic number*. With three exceptions these numbers are simply the serial number of the elements, beginning  $H = 1$ ,  $He = 2$ ,  $Li = 3$ , etc. We shall see later on that they have a very important and fundamental significance.

**Two families in a group.** A study of the elements comprised within a group discloses a further fact of much interest. As we have seen, the relationship between the corresponding elements in the first two series is a very close one. Below this point the elements in each group (excepting in Group 0) fall very naturally into two sub-groups, called *families*. In the table these are designated as *A* and *B*. The elements in one family resemble each other much more closely than they do those in the other family in the same group. Thus, in Group II, calcium, strontium, barium, and radium form one family of very similar elements, while zinc, cadmium, and mercury constitute the other.

The first two rows (or series), which include the 16 elements of smallest atomic weight, do not fall distinctively into either family in their group, but combine the properties of both families. So they stand as types of the general characteristics of their groups.

**Long and short series.** It will be noticed that, following the two series of type elements, each *odd-numbered* series consists of elements in family *A*. This is followed by a group of 3 elements in Group VIII, and then by an *even-numbered* series consisting of elements exclusively in family *B*. This order is

repeated three times. The first two rows of 8 elements each (series 1 and 2) are called *short series*. A row consisting of 8 elements in family *A*, 3 elements in Group VIII, and 7 elements in family *B* (18 elements in all) is called a *long series*.

**Thomsen's table.** The Danish chemist Thomsen suggested an arrangement of the periodic table which, with a number of modifications, is shown below. Hydrogen and helium form a first row of two elements. This is followed by the two short series of 8 elements each. Then follow the three long series of 19 elements each, and an incomplete fourth row. The diagonal lines connect the elements of the short series with the two families of their groups. In this table *those elements that are most intimately related fall in the vertical columns formed by the long series*.

THOMSEN'S TABLE OF THE ELEMENTS

																		H		He																			
																		1		2																			
																		Li	Gl	B	C	N	O	F	Ne														
																		3	4	5	6	7	8	9	10														
																		Na	Mg	Al	Si	P	S	Cl	A														
																		11	12	13	14	15	16	17	18														
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr																						
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36																						
Rb	Sr	Y	Zr	Cb	Mo	—	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe																						
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54																						
Cs	Ba	La <sup>1</sup>	Ce	Ta	W	—	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	—	Nt																						
55	56	57	58	73	74	75	76	77	78	79	80	81	82	83	84	85	86																						
—	Ra	Ac	Th	UX <sub>3</sub>	U																																		
87	88	89	90	91	92																																		

<sup>1</sup> The rare earth elements, 57-72 (one of which is unknown), would constitute another row nearly across the table, but in chemical properties they do not fit into the vertical columns and are omitted from this table.

**Group resemblances.** In any one group the elements have much the same valence characteristics. They may therefore be expected to form oxides, hydroxides, acids, and salts of the same general formula. The hydrides and oxides of maximum valence are indicated by the formulas at the top of the columns (p. 385). It will be seen that the valence toward oxygen increases from 0 in Group 0 to 8 in Group VIII, while that toward hydrogen reaches a maximum in Group IV. For example, sulfur, in the sixth column, has an oxygen valence of 6, as shown in the oxide of the formula  $\text{SO}_3$ , while its valence toward hydrogen is 2, as indicated in the formula  $\text{H}_2\text{S}$ . It usually happens that, in addition to the oxide normally characterizing a group, each element forms other oxides not forecast by the table.

**Family resemblances.** The resemblances of the members of a family to each other are more marked and extend not only to the general chemical characteristics but to physical properties as well. There is, in most cases, a regular variation in any given property as we pass from the member of smallest atomic weight to that of largest, so that the middle one is a mean between the others. This is true in regard to chemical activity and such properties as melting point, boiling point, density, color, solubility of parallel salts, and many similar properties. These points will be dwelt upon in the several families as they are taken up in order.

**Irregularities in the table.** Notwithstanding the many very striking relations suggested by the periodic grouping, it contains a number of imperfections and anomalies.

1. In the first place, the relations are only qualitative in character. The atomic weights themselves do not differ regularly from element to element, the difference in some cases being very small, as between cobalt and nickel, while in others it is as much as four units, as between calcium and scandium. The same irregularity characterizes all the relations represented in the table, so that no property of one element can be calculated exactly from the known magnitude of the same property in another element.

2. A most striking fact is that there is no place in the table for hydrogen, one of the most important of all the elements. It seems to stand quite alone and to have no close relation to any other element. It certainly does not belong in Group 0, for it has very pronounced chemical activity. All its physical characteristics as a gas would exclude it from Group I, which is composed of typical metals. It forms positive ions in solution, and it is in this respect only that it suggests metallic properties.

3. In a few cases the order in which two elements are placed in the table is not in keeping with the magnitude of their respective atomic weights. Thus argon and potassium have been reversed in the table, in order that they may fall in the columns where they undoubtedly belong. The same is true of tellurium and iodine, and of nickel and cobalt. While it is possible that the values of these weights are imperfectly determined, they have been the subject of so many researches that it does not seem probable that they will be greatly changed.

4. The last column in the table has little meaning at present, though there is a certain regularity in the periodic reappearance of sets of three closely similar elements at the end of alternate series, and some regularities can be traced between corresponding members of these sets.

5. The periodic arrangement places sodium, copper, silver, and gold together in one family, whereas there is not much resemblance in the chemistry of any of these elements. They are also placed in the family of unit valence, although both copper and gold usually have a higher valence.

6. One of the most irregular features of the grouping is in connection with a series of elements known collectively as the rare earth metals. It will be noticed that, in the third group and the seventh series, beside the symbol La there is a reference <sup>(1)</sup> that leads to a footnote explaining that between barium and tantalum there are sixteen rare elements, or almost enough to constitute a long series. Yet each of these elements has a valence of 3, and they are so very similar that they can hardly be separated

at all. Evidently they all belong in the same family and should not be distributed throughout the other families, to which they have little or no resemblance. Cerium alone possesses properties which warrant placing it in a different group (the fourth). It would seem that throughout these sixteen elements the normal increase in atomic weights is attended with no appreciable change in chemical character. The regular order is then resumed when tantalum is reached.

**Meaning of imperfections.** That some very fundamental relations are represented in the periodic table cannot be doubted. It can hardly be mere chance which, on arranging the elements in accordance with their atomic weights, brings into the same group those which have long been recognized as intimately related. At the same time the unquestioned irregularities in the table suggest that the present arrangement is far from perfect. Many attempts have been made to improve upon the plan of arrangements, and some of the proposed plans are very interesting and suggestive, especially those in which the elements are arranged on a spiral curve, or a helix. A diagram showing such an arrangement will be found in the Appendix.

**Value of the periodic law.** While admitting that the table contains many imperfections and will doubtless undergo many modifications, it is nevertheless of very great service to us.

1. It is a constant check on experimental work. If a given piece of work results in values which are not in harmony with the table, attention is at once directed to the value, and it is very carefully verified. Thus it was at one time announced that the density of pure cæsium was 2.4. This value was higher than would be expected from the values for potassium and rubidium, and a careful redetermination gave the value 1.87.

2. The service of the table can best be seen by going back to the time before the periodic law was formulated. There was then no guide at all as to probable values, and one value for a physical or chemical property was as reasonable as any other. When Mendeléeff first arranged the table, a number of elements

were plainly out of place, and many of their physical constants were out of keeping with the position of the element. In almost every case a careful study showed that the atomic weight was wrong or the property erroneously determined, the revised values coming into harmony with the table.

3. The table has also been of value in forecasting the discovery of new elements, together with their probable character. In one or two cases it has even been possible to predict in what kind of mineral they would probably be found. In arranging the table it was found necessary to leave certain positions blank, in order that the next element should fall in the column where it evidently belonged. These blanks were obviously the positions of undiscovered elements, and from their position and the character of the elements on each side of them their properties could be in a measure predicted. In this way Mendeléeff was able to predict the properties of scandium, gallium, and germanium before they were discovered. Some blank spaces still remain, and two have been filled in recent years by the discovery of radium and niton.

4. On the other hand, the table has been of much service in ruling out a number of elements for which there was no place. Many of these have been described from time to time, and as soon as it was seen that there was no place for them, they became the center of much interest. This resulted in more extended study, and experiment soon showed that the supposed element was not entitled to such a rating.

5. The very fact that the table is imperfect has stimulated a vast amount of careful work, to secure more accurate results on the constants of the elements, so that a more perfect generalization may be reached. A law that undoubtedly states a truth, yet has marked exceptions, always suggests new experiments. At the present time the atomic weights are being redetermined with a care never before devoted to them, and constants of other kinds, such as melting and boiling points, densities, and compression coefficients, are also undergoing revision.

6. Finally, from the standpoint of convenience the table is of much service in assisting the memory. When the general character of the relations between the elements is understood, one is reasonably safe in assuming that in all probability a given element will have about the properties suggested by its position. Such an assumption is always open to doubt, but if merely general points are involved, and not quantitative relations, the assumption is usually borne out by the facts.

### THE STRUCTURE OF THE ATOM

**Evidence for atomic complexity.** A number of facts have been presented in earlier pages that make it certain that the atoms cannot be minute homogeneous particles, like small shot, but have a rather elaborate structure.

1. *Valence.* It is difficult to see why one atom of hydrogen is unable to unite with more than one atom of any other kind, while one atom of oxygen has a valence of 2, and an atom of carbon of 4. It cannot be due to size or weight, for the univalent atom caesium has a high atomic weight, while carbon with a valence of 4 is one of the lightest of atoms. There must be something in the *structure of the atom* to explain valence.

2. *Ionization.* We have seen that modern methods of physics have demonstrated that electricity is atomic in nature, and that the most plausible theory of electrical conduction in solution is based on the idea that certain atoms can suffer a loss of electrons (atoms of electricity), while others can take up an excess of electrons.

3. *Periodic law.* The periodic law lends strong support to the view that atoms are complex. It is difficult to see why a recurrence of a set of physical and chemical characteristics should take place at regular intervals as the atomic weight increases, unless it be that this increase of weight occasions a recurrence of some type of architecture in the atoms. All atoms having the same general style of architecture or structure will very naturally have many properties in common.

4. *Atomic weights approximately whole numbers.* The mere fact that so many of the atoms have weights that are *very close to whole numbers* is strongly suggestive that the atoms are multiples of some one unit. On the theory of chances we can calculate that the chances against this being merely accidental are so great as to constitute proof that there is a natural reason for this regularity. If we omit magnesium, silicon, and chlorine from the first 24 elements, the average weight of the remaining 21 deviates only 0.05 from whole numbers. These exceptional elements will be discussed later.

**Prout's hypothesis.** As early as 1815 and upon the basis of very imperfect experiment, an English physician named Prout advanced the idea that

the atomic weights of all the elements are exact multiples of that of hydrogen and that the atoms of the various elements have been formed by some sort of condensation of hydrogen atoms.

The most careful determinations of atomic weights have always shown that Prout's hypothesis cannot be wholly true, for the atomic weights are not exact multiples of any one number. Nevertheless the unmistakable tendency to approach whole numbers, especially on the basis of  $O = 16$  rather than  $H = 1$ , indicates that there is some measure of truth in this early guess as to the nature of atoms.

**Discoveries relating to atomic structure.** Two great lines of investigation, connected with physics rather than with chemistry, have supplied the missing clues as to the real nature of atoms. A knowledge of physics is necessary for a complete understanding of these discoveries, and a mere sketch only can be given here.

1. *Discharge in a vacuum tube.* In a general way a tube for the study of an electrical discharge through rarefied gases is constructed as in Fig. 99. It consists of a glass tube provided with electrodes *A* and *B*, and a side tube *C*, by which the air or other gas can be pumped out to any desired extent. At a moderately high vacuum a discharge between the electrodes can be secured by application of a high-voltage current to the electrodes. In such a discharge three facts have been proved that are of great interest to us.

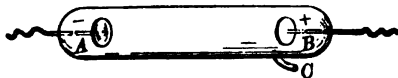


FIG. 99

(a) From the cathode *A* minute bodies called *cathode rays* are shot off, that (1) are negatively charged, (2) move with very high velocity, (3) are all alike in mass and charge irrespective of the nature of the gas in the tube or of the electrodes, (4) have a mass equal to  $\frac{1}{1844}$  of the mass of a hydrogen atom, and (5) have an electrical charge equal to the charge on a univalent ion, such as  $Cl^-$ .

(b) From the anode *B* much larger particles called *canal rays* are shot off, that (1) are positively charged, (2) are of ordinary atomic size, never smaller than a hydrogen atom, and (3) in mass depend upon the nature of the gas in the tube.

(c) From the point in the tube where the cathode rays strike, and because of their impact, there proceeds in all directions a very intense radiation, consisting of waves in the ether like those of light, but in wave length about 1000 times shorter than the waves of light. They are, of course, invisible to the eye, but they affect a photographic plate very actively. They are called *X-rays* and have become well known popularly through their use in X-ray photography.

*An X-ray tube.* In an X-ray tube (Fig. 100) the cathode is concaved in such a way as to focus the cathode rays at a definite point *B* within the

tube. A metal plate fixed at this point (known as a target, or anti-cathode) and inclined at a suitable angle becomes the source of radiation for the

X-rays (C) that pass out through the glass in every direction.

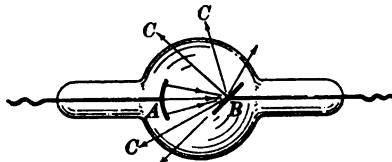


FIG. 100

*Crystal structure.* The student will recall that when a fine pencil of light shines through dusty air, each dust particle scatters, or *diffracts*, light, and so itself becomes a source of light waves. If the dust particles have a smaller diam-

eter than the length of the waves of light, they cease to diffract the light in this way. The atoms in a crystal are, of course, much too small to diffract light.

It occurred to the Swiss scientist Laue that the very short X-ray waves might be diffracted by *atoms*, just as the ordinary light waves are diffracted by *dust particles*. A fine pencil of X-rays shining through a crystal upon a photographic plate behind it would, in general, pass straight through and affect merely a spot on the plate. But those waves that encounter an atom in the crystal would be diffracted.

Now we have supposed that the atoms in a crystal are arranged in regular positions. If each of these becomes a center of radiation, the waves proceeding from these numerous centers will, in general, destroy each other. But some will *reënforce* each other (when like phases coincide) and these reënforced waves will strike the photographic plate at some distance from the central spot. Since the atoms are arranged in a regular way, the secondary spots on the photographic plate will have the same relative arrangement as the atoms themselves.

A photographic plate that has been so exposed and developed is shown in Fig. 101. The large central spot caused by the direct pencil of rays is surrounded by a series of small spots produced by waves diffracted by atoms in *fixed positions in the crystal*. From the arrangement of these spots a skillful geometer can construct a space model

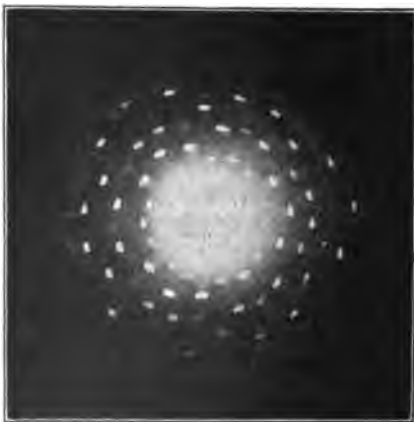


FIG. 101

showing how the atoms must be arranged in the crystal to produce the spots. Fig. 102 shows such a model of a crystal of common salt in which the dark spots represent sodium atoms and the light ones chlorine atoms. In this way we are able actually to photograph the arrangement of the atoms in a crystal. For the development of the ideas of Laue we are largely indebted to W. H. and W. L. Bragg (father and son), who employed crystal surfaces for diffracting X-rays, just as we employ diffraction gratings with ordinary light waves in spectroscopic work.

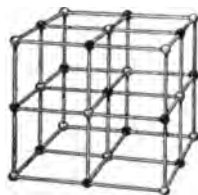


FIG. 102

*State of molecules in a crystal.* It will be noticed that the crystal model represents each atom of the molecules to be spaced at a distance from every other atom, so that each sodium atom is symmetrically spaced in reference to a number of chlorine atoms. The molecules as such have lost their identity and have been resolved into individual atoms, or radicals, so that in a sense each crystal is one huge molecule. If the crystal is *dissolved*, or *melted*, the atoms and radicals form ions and to some extent reunite as simple molecules.

*Atomic number.* As we have seen, X-rays are started by the impact of cathode rays concentrated upon some target, and it has been found that their wave length *depends upon the nature of the material constituting the target*. A brilliant young English physicist, Moseley (who died fighting as a private in the trenches of Gallipoli) studied the X-ray spectra produced by different targets, using a crystal as a diffraction grating. He found that all elements, when used as targets, produce an X-ray spectrum of exactly the same type, consisting of a few lines only; but that as the atomic weight increases, the whole group of lines shift toward the region of shorter wave lengths. When the elements were arranged in the order of increasing atomic weight (as targets), *the shift was always of the same magnitude as we pass from element to element*. Having established this fact, it is possible to show exactly where each element belongs in the series of elements by measuring the shift it produces in the X-ray spectrum. The position in the series of elements determined in this way is called the *atomic number* of the element.

The atomic number and the atomic weight place the elements in the same order *with three exceptions*. The atomic number reverses the order of the atomic weights in the case of potassium and argon, of tellurium and iodine, and of cobalt and nickel. We have already seen that the chemical characteristics of these three pairs of elements require us to reverse their order to fit them into the periodic table in the groups in which they plainly belong. The atomic number is therefore more reliable than the atomic weight in determining the properties of an element.

2. *Facts of Radioactivity.* The spontaneous changes taking place in the atoms of the elements uranium and thorium will be described more fully in a later chapter. At this point it is sufficient to say that from time to time atoms of these elements explode, and as products of these explosions we find three things that are either identical with the three things we have found in the discharge of vacuum tubes, or are extremely similar to them. They were originally called  $\alpha$ -rays,  $\beta$ -rays, and  $\gamma$ -rays.

The  $\alpha$ -rays resemble canal rays in being charged positively, and in being of atomic size. They differ from them in that they all have a mass of 4 and have been found to be identical with atoms of helium, save that each one carries two positive charges. The  $\beta$ -rays are the same as the cathode rays, and are now called *electrons*. The  $\gamma$ -rays are the same as the X-rays, but are of much shorter wave length.

**Theories of structure of the atom.** With the facts described in the foregoing paragraphs before us, we may begin to formulate a very definite theory of atomic structure. It is clear, however, that it will not be a simple theory, and that we are merely at the beginning of what will doubtless be a very wonderful conception when it is complete.

1. *Physical theories.* Those most interested in physical studies have formulated theories which in general include the following ideas: (a) Each atom possesses a central nucleus the exact nature of which is not very clearly imaged, but which is positively charged and in which nearly all the mass of the atoms is situated; (b) a number of electrons revolve around this nucleus somewhat as planets revolve around a central sun; (c) each element has a different nucleus and a different number of satellite electrons; (d) the number of electrons in a given atom is equal to the atomic number of the element. J. J. Thompson and Bohr have been most active in developing these physical theories.

2. *Chemical theories.* The chemist finds it difficult to harmonize the known facts of chemistry with the idea of *revolving* electrons. There are hundreds of cases known in which two compounds are made up of the same number and kinds of atoms and yet have wholly different properties; and this fact seems to demand that the atoms shall be held in fixed positions with reference to each other. Moreover, the simple facts of valence can hardly be explained on the basis of freely moving electrons. Accordingly, the chemist thinks of the electrons as occupying *fixed positions* about the central positive nucleus, or at least positions that do not change in relation to each other. We owe most of our ideas of the details of this distinctively chemical theory to the American chemists G. N. Lewis and Irving Langmuir.

Evidently there cannot be two different theories of atomic structure that are both true pictures of the reality. In time we shall see these two united into one comprehensive theory.

**Details of the chemical theory.** (1) Each atom has a nucleus made up of positively charged units which constitute nearly all the mass of the atom. (2) For each positive unit in the nucleus there is a negative electron located at some distance from the nucleus. (3) The number of both positive and negative units in the atom is equal to the atomic number. (4) The negative electrons tend to assume *definite symmetrical positions around the group of positive units that constitutes the nucleus.*

TABLE OF FIRST TEN ELEMENTS

ELEMENT	+ UNITS	- UNITS	ELEMENT	+ UNITS	- UNITS
Hydrogen . . .	1	1	Carbon . . .	6	6
Helium . . . .	2	2	Nitrogen . . .	7	7
Lithium . . . .	3	3	Oxygen . . . .	8	8
Glucium . . . .	4	4	Fluorine . . .	9	9
Boron . . . . .	5	5	Neon . . . . .	10	10

**Helium atom completely symmetrical.** The helium atom with its two units of each kind constitutes a perfectly symmetrical grouping, illustrated in Fig. 103. The two electrons (o) take up positions polar to the two positive units at the center. Either loss or gain of an electron would break up this symmetry, and this accounts for the chemical inactivity of helium and its failure to form molecules from its own atoms.



FIG. 103

**Formation of positive ions.** In atoms with 3, 4, or 5 electrons there is no very symmetrical plan of grouping of electrons around the central positive nucleus. These atoms tend to lose electrons until only two are left in the polar position about the nucleus as in the helium atom. This will give the arrangements illustrated in Fig. 104. The positive signs outside the circle indicate the excess units in the nucleus over the two electrons that remain.



FIG. 104

It will be seen that these diagrams correspond to the ions  $\text{Li}^+$ ,  $\text{Gl}^{++}$ , and  $\text{B}^{+..}$ . These *ions*, therefore, resemble the helium atom, save that they have an increasing number of positive units in the nucleus and therefore an increasing weight.



FIG. 105

The hydrogen atom has but a single unit of each kind, and this gives no symmetrical grouping. Accordingly, the hydrogen atom tends to lose its electron, but the remaining nucleus consists of but a single positive unit and so differs from all other ions in structure. Two hydrogen atoms together form a grouping almost like that of helium (Fig. 105), and this explains the stability of the hydrogen molecule.

**Formation of negative ions.** The most stable type of atom after we pass helium is the atom consisting of a nucleus of 10 positive units, 2 electrons in polar position, and 8 electrons at a greater distance in symmetrical positions. These 8 electrons will be at the 8 solid angles of a cube and are said to constitute the *outer shell* of the atom as shown in Fig. 106. The central arrangement is very similar to the helium atom, save that there are 10 positive units instead of 2. Any loss or gain of electrons will destroy the symmetry of the grouping, so the atom should be very inactive like helium and not disposed to form molecules. Reference to the table will

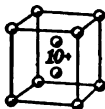


FIG. 106

show that it is the *neon* atom, the close homologue of helium.

The atom just before neon, fluorine, has one less unit of each kind, namely, 9. It may be represented by Fig. 107. One solid angle in the outer shell has no electron, and this atom has a strong tendency to get hold of an extra electron for this position, even if it has to rob some other atom to get it. Now we have seen that the atoms H, Li, and Cl easily give up electrons. The fluorine atom will take an electron from any of these and so complete its cube. This will then be very much like neon in properties, save that it has one electron in excess of its nuclear positive charge, and so as a whole it will have an attraction for any positively charged group like a positive ion and tend to hold it in rather feeble combination. It is the fluorine ion ( $F^-$ ).

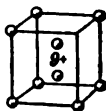


FIG. 107

**Chemical combination.** If there is no dissociating solvent present to exercise a field of force to part the ions whose formation we have pictured, a positive and a negative ion will tend to be attracted to each other with a force sufficient to keep them together in rather feeble combination. This may be made clear by an illustration.

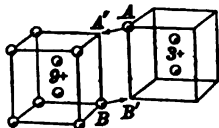


FIG. 108

1. If a lithium atom approached a fluorine atom (in the absence of a dissociating solvent), the one electron in the outer shell of the lithium atom is attracted to the unoccupied position in the outer shell of the fluorine atom, pulling the whole lithium atom with it. As shown in Fig. 108, the electron *A* moves to the position *A'*, the electron being shared by both cubes. This brings the electron *B* close to the position *B'*, so that the electron *B* is also shared by both cubes, as shown in Fig. 109. This mutual sharing of two electrons constitutes a univalent union as expressed in the ordinary formula  $Li-F$ . In more compact form the space formula may be written thus,  $:\ddot{F}:Li$ . Owing to the tendency to round out cubical forms, Lewis has called this the *Cubical Theory*, and Langmuir the *Octet Theory*.

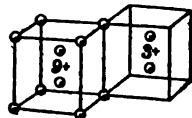


FIG. 109

It will be seen that an atom like lithium, with only one detachable electron, has no octet arrangement around the nucleus, but merely an electron at some distance from the central grouping. However, it assists the imagination to sketch the outline of the octet with unoccupied corners, as has been done in these diagrams.

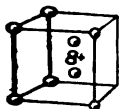


FIG. 110

2. The mutual attraction of the two atoms may be so great that there is little tendency to part into ions after combination. This may be illustrated in the case of many oxides.

With oxygen we have the atom shown in Fig. 110. There are two electrons lacking at solid angles of the outer shell, or cube octet, and the oxygen atom will therefore tend to attract two electrons from atoms that easily surrender them. Suppose an atom of glucinum comes along with two electrons *A* and *B* (Fig. 111) in its outer shell. These are attracted to the vacant corners *A'* and *B'*. On this line as a hinge (Fig. 112) the two cubes move as closely together as possible, and this brings points

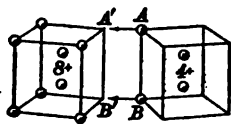


FIG. 111

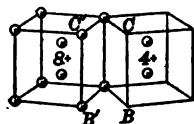


FIG. 112

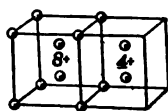


FIG. 113

*C*, *C'* and points *B*, *B'* into coincidence, as shown in Fig. 113 or, more briefly, in the formula  $\ddot{O} :: Gl$  or  $O = Gl$ . The double bond is thus equivalent to having four electrons in common by the two atoms.

**Atoms with two shells.** When we pass to atoms of higher atomic number than 10 (neon), the positive units continue to concentrate at the center as a nucleus, but the additional electrons form a new shell outside of the completed octet, and the whole process repeats itself. Thus Fig. 114 will present a picture of the chlorine atom. Just as with fluorine, one electron is lacking in the outer shell, and this brings about the close resemblance of chlorine to fluorine. *It is the electrons on the outer shell only that determine the chemical conduct of the element, the completed inner shells having relatively small influence.*

**The positive nucleus.** We have seen that the mass of the atom (save the negligible fraction due to the electrons) is all concentrated in the nucleus. Since this is built up of unit positive charges, it seems reasonable to suppose that each positive charge will be associated with the same mass, and that the mass of all atoms will be multiples of the mass associated with the unit positive charge. We have seen that this is nearly true (Prout's hypothesis) but not absolutely so.

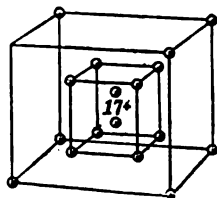


FIG. 114

The fact that helium is given off in some atomic disintegrations suggests that this is at least one of the fundamental units in the nucleus. Since the weight of the helium atom is 4, multiples of helium would account for those elements only whose weights are multiples of 4.

The American chemist Harkins has suggested that the nucleus of all elements is made up of *helium* and *hydrogen* atoms. By the action of  $\alpha$ -rays (from radium) on nitrogen gas, Rutherford has obtained evidence pointing to the decomposition of nitrogen atoms into helium and hydrogen. This would indicate that the nucleus of the nitrogen atom is made up of  $3 \text{ He} + 2 \text{ H}$ . To account for the deviations in weight for multiple numbers of these two atoms, Harkins assumes that in condensing to form a nucleus, the weight of these constituent atoms suffers a slight but nearly constant loss. This *packing effect*, as he terms it, amounts to almost exactly 0.77 per cent for the great majority of atoms, especially for those of relatively small atomic weight.

**Summary.** To go further is much beyond the scope of this book. From what has been said the student will see that we have in the octet theory the beginnings of a theory that has already supplied an astonishingly interesting explanation of many things that have long puzzled chemists. It is not too much to assume that the theory in its present form is the beginning of one of the most fundamental conceptions of chemistry.

### QUESTIONS

1. What is meant by the statement that the relations of the periodic table are only qualitative?
2. Can you discover any other triads similar to those of Döbereiner?
3. What metallic and what nonmetallic elements have been studied up to this point?
4. Can you think of any occurrences in nature or in machinery that are periodic in character?
5. Distinguish between a short series and a long series.
6. Can you predict any properties for the element of atomic number 84?
7. What would be the structure of the sodium atom? of the chlorine atom?

## CHAPTER XXI

### THE CHLORINE FAMILY

NAME	ATOMIC WEIGHT	MELTING POINT	BOILING POINT	COLOR AND STATE
Fluorine (F) . . . . .	19.00	- 223°	- 187°	Pale-yellowish gas
Chlorine (Cl) . . . . .	35.46	- 101.5°	- 38.6°	Greenish-yellow gas
Bromine (Br) . . . . .	79.92	- 7.3°	68°	Red liquid
Iodine (I) . . . . .	126.92	113.5°	184.4°	Purplish-black solid

**NOTE.** Chlorine, the element which gives its name to the family of elements now to be discussed, has already been described along with hydrochloric acid in Chapter XIII, and the student should review this chapter along with the study of the present one. In connection with the discussion of the characteristics of the family, it is desirable to mention again certain properties of chlorine for the sake of comparison with the properties of the other elements of the family.

**Characteristics of the family.** The four elements named in the table form a strongly marked family and illustrate very clearly the way in which the members of a periodic family resemble each other, as well as the character of the differences which we may expect to find among the several individuals. Before taking up a discussion of each of these elements, it is desirable to discuss the group as a whole, pointing out the relation which the properties of the individual members bear to each other, as well as the character of some of their compounds.

1. **Occurrence.** Because of their great activity these elements do not occur in the free state in nature. Their compounds, however, are very abundant, those of chlorine, bromine, and iodine being found especially in sea water. The most abundant of these is sodium chloride, or common salt. Because the other elements of the family form compounds resembling common salt, they are often termed the *halogens*, a word meaning "producers of salt."

2. *Properties.* In connection with the periodic law it was pointed out that the elements constituting a family exhibit a more or less regular gradation of properties. In the case of the elements of the chlorine family this characteristic is readily observed by reference to the table. It will be seen that the melting points and boiling points of these elements are in the same order as their atomic weights. A somewhat similar gradation is noted in the color of the elements, as well as in their physical states. Thus, while both fluorine and chlorine are gases, chlorine is much more readily condensed and has a much deeper color than fluorine; bromine is a brownish-red liquid, while iodine is a purplish-black solid. A similar gradation of properties is noted in their chemical conduct. For example, the affinity of these elements for hydrogen and metals under the same conditions is in the reverse order of their atomic weights, being greatest in the case of fluorine and least in the case of iodine. It follows that the compounds of fluorine with hydrogen and metals are in a general way the most stable, while the corresponding compounds of iodine are the least stable.

The affinity of the elements of the family for oxygen is very slight. The most stable oxide of the group is iodine pentoxide ( $\text{I}_2\text{O}_5$ ), and even this is decomposed with ease. Chlorine forms three oxides ( $\text{Cl}_2\text{O}$ ,  $\text{ClO}_2$ , and  $\text{Cl}_2\text{O}_7$ ), all of which are very unstable. No oxides of fluorine or bromine are known.

3. *Compounds with hydrogen.* Hydrogen combines with each of the elements of the family to form the following important compounds:

Hydrogen fluoride ( $\text{H}_2\text{F}_2$ ), a colorless liquid boiling at  $19.4^\circ$

Hydrogen chloride ( $\text{HCl}$ ), a colorless gas condensing to a liquid at  $-83.1^\circ$

Hydrogen bromide ( $\text{HBr}$ ), a colorless gas condensing to a liquid at  $-69^\circ$

Hydrogen iodide ( $\text{HI}$ ), a colorless gas condensing to a liquid at  $-34.1^\circ$

These compounds, in the complete absence of water, are rather inactive and have neither acid nor basic properties. They dissolve in water, however, forming solutions that are acid in character. These solutions are known respectively as hydrofluoric,

hydrochloric, hydrobromic, and hydriodic acids. Hydrofluoric acid is rather weak, but the three remaining ones are among the strongest known. The salts of these acids are known respectively as fluorides, chlorides, bromides, and iodides.

In their compounds with hydrogen and the metals, the halogens are univalent. In their oxides, chlorine and iodine have a much higher maximum valence, chlorine being apparently heptavalent in the oxide  $\text{Cl}_2\text{O}_7$ .

### FLUORINE

**History and occurrence.** The most common forms in which fluorine occurs in nature are the minerals known respectively as fluorite, cryolite, and fluorapatite. *Fluorite*, also known as fluorspar, is calcium fluoride ( $\text{CaF}_2$ ). It is widely distributed and is found in large quantities, especially in Illinois. *Cryolite* is a fluoride of sodium and aluminium ( $\text{Na}_3\text{AlF}_6$ ) and is found in Greenland and Iceland. *Fluorapatite* is the most abundant of the three and consists apparently of calcium fluoride combined with calcium phosphate, as represented in the formula  $3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaF}_2$ . Traces of compounds of fluorine are also found in sea water, in many minerals, in bones, and in the enamel of the teeth.

While the compounds of fluorine have long been known, all efforts to liberate the element failed until the year 1886, when the French chemist Moissan finally succeeded in isolating it and made an extended study of its properties.

**Preparation.** Because of its great activity, fluorine cannot be prepared by any of the general methods which serve for the preparation of the other members of the chlorine family. Moissan finally isolated it by the electrolysis of hydrogen fluoride. Pure hydrogen fluoride, like pure water, is not an electrolyte. As in the case of water, it may be made an electrolyte by dissolving in it an appropriate compound. For this purpose Moissan used potassium hydrogen fluoride ( $\text{KHF}_2$ ), a solid that is readily

obtained in a pure condition. Since hydrogen fluoride boils at  $19.4^{\circ}$ , the operation must be carried out at a low temperature, to prevent the liquid from vaporizing. On passing a current of electricity through the solution, hydrogen is evolved at the cathode and fluorine at the anode.

**Moissan's method.** The solution of potassium hydrogen fluoride in hydrogen fluoride was introduced into a U-shaped tube *A* (Fig. 115) made of platinum. The tube was fitted with calcium fluoride stoppers *B, B*,

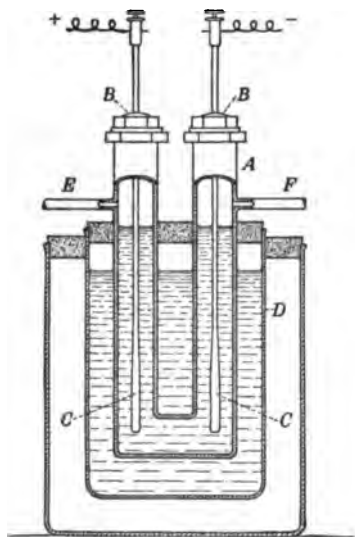


FIG. 115

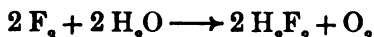
through which passed wires attached to electrodes *C, C*, made of an alloy of platinum and iridium, which is very resistant to the action of reagents. The tube containing the solution was placed in a vessel (*D*) filled with a low-boiling liquid, which, by its rapid evaporation, reduced the temperature sufficiently to prevent the vaporization of the hydrogen fluoride. On electrolyzing the solution, fluorine was evolved at the anode and escaped through the tube *E*, while the hydrogen evolved at the cathode escaped through the tube *F*. Moissan found later that copper is but slightly attacked by fluorine, and that a copper tube could therefore be used in place of the more expensive platinum tube.

**Preparation from potassium hydrogen fluoride.** Experiments carried out under the direction of the Federal government during the World War

demonstrated that fluorine can be prepared with comparative ease. It is only necessary to melt potassium hydrogen fluoride ( $\text{KHF}_2$ ) in a copper vessel of suitable design and subject it to electrolysis.

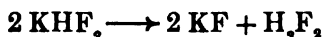
**Properties.** Fluorine is a gas, pale yellow in color. It is 1.3 times as heavy as air. It can be obtained in the form of a yellow liquid which boils at  $-187^{\circ}$  and solidifies at  $-223^{\circ}$ . Chemically it is one of the most active of all elements. Most of the metals and many of the nonmetals, when brought in contact with fluorine, combine with it so rapidly as to produce light. It

unites with hydrogen with explosive violence and readily abstracts it from its compounds. For example, it decomposes water violently, forming hydrogen fluoride and oxygen :

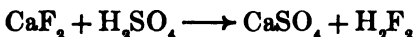


From 10 to 14 per cent of the oxygen liberated is at the same time converted into ozone. It liberates all the other members of the chlorine family from their compounds with hydrogen and the metals. It does not combine with oxygen, however, and gold, platinum, and copper are but slightly attacked by it.

**Hydrogen fluoride ( $\text{H}_2\text{F}_2$ ).** Pure hydrogen fluoride is best prepared by heating anhydrous potassium hydrogen fluoride :

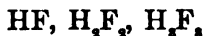


The process must be carried out in platinum vessels. Hydrogen fluoride can also be prepared by the action of sulfuric acid on the fluorides of the metals. Calcium fluoride, being the cheapest, is always used :

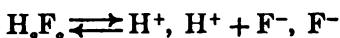


The operation is carried out in vessels of platinum or lead. This is the method commonly used in the preparation of its aqueous solutions, in which form it is ordinarily used.

**Properties.** Hydrogen fluoride is a colorless liquid that boils at  $19.4^\circ$ . Its vapor is lighter than air. At low temperatures it forms a white solid melting at  $-92.3^\circ$ . An aqueous solution containing 85 per cent of the compound has a constant boiling point, namely  $120^\circ$ , and distills with unchanged concentration (p. 179). As indicated by the formation of such acid salts as  $\text{KHF}_2$ , its formula is generally regarded as  $\text{H}_2\text{F}_2$ , although at different temperatures it may exist in any of the forms indicated by the formulas

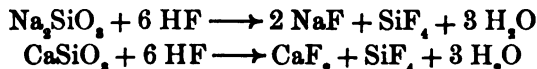


**Hydrofluoric acid.** Pure hydrogen fluoride is a nonconductor of electricity and is neutral in reaction. When dissolved in water it ionizes as follows:



The resulting solution is acid in character and is known as *hydrofluoric acid*. The acid is usually given the simple formula HF. Ordinary commercial hydrofluoric acid contains about 50 per cent of hydrogen fluoride. Since this solution readily attacks glass, it is kept in bottles made of a wax derived from petroleum and known as ceresin.

Hydrofluoric acid is a rather weak acid and possesses all the characteristics of such a compound. It acts upon some of the metals, as well as upon their oxides and hydroxides, forming the corresponding salts. A distinguishing property of hydrofluoric acid is its action upon glass. Ordinary glass consists principally of sodium silicate ( $\text{Na}_2\text{SiO}_3$ ) and calcium silicate ( $\text{CaSiO}_3$ ). Hydrofluoric acid reacts with these silicates, forming fluorides of sodium and calcium, while the silicon also combines with fluorine to form silicon tetrafluoride, a gaseous compound having the formula  $\text{SiF}_4$ :



Advantage is taken of this reaction in marking thermometers and flasks, as well as in etching designs on glassware.

Hydrofluoric acid is exceedingly corrosive. A single drop in contact with the skin produces a very painful wound, slow to heal. Its vapor must not be inhaled.

**Etching glass.** The etching property of the acid may be shown in the following way: A piece of glass is covered with a thin coating of some wax, such as paraffin. To do this the wax is melted on the glass, which is then tipped until the melted wax completely covers it with a thin film. After the wax hardens, any desired design is made by cutting through the wax with a fine metal point. The object so prepared is then exposed to the fumes of hydrofluoric acid. The acid attacks the glass wherever exposed, destroying its luster and leaving the design etched upon its surface.

**Salts of hydrofluoric acid; the fluorides.** The fluorides of most of the metals are known. They can be prepared by the usual method for preparing salts, namely by the action of the

acid upon the metal directly or upon their oxides or hydroxides. The most important of these salts is the well-known *calcium fluoride*, or fluorite, as it is termed when found in nature. A number of the univalent metals form acid salts such as  $\text{KHF}_2$ .

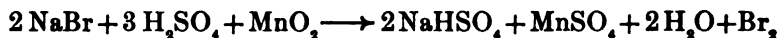
### BROMINE

**Occurrence and history.** Bromine occurs in nature combined with certain metals, principally sodium, potassium, calcium, and magnesium. These compounds are known as *bromides*. Large quantities of bromides are found in the famous potash deposits at Stassfurt, Germany (p. 541). They also occur in the waters of many springs, especially in Michigan and Ohio, mixed with relatively large quantities of sodium chloride. When such waters are evaporated, the sodium chloride separates first, since it is present in much larger quantities and is less soluble than the bromides. The liquor remaining after the separation of most of the sodium chloride is known as the *mother liquor*, and contains the bromides in solution. It was from this liquor that the German chemist Liebig first isolated bromine. He concluded, however, that the red liquid which he obtained was simply a compound of chlorine and iodine. A few months later (1826) the French chemist Ballard again obtained the substance from similar liquors. He rightly considered it to be an elementary substance, and, because of its disagreeable odor, named it *bromine*, a word meaning "stench."

**Preparation.** The general methods used in the preparation of chlorine (p. 191) may likewise be employed in separating bromine from its compounds. The laboratory and commercial methods most largely used are the following:

1. *Laboratory method.* In the laboratory, bromine is most often prepared by the action of oxidizing agents upon hydrogen bromide. It is convenient to generate the hydrogen bromide in the course of the reaction by using a mixture of sodium bromide and sulfuric acid. The oxidizing agent ordinarily used

is manganese dioxide. The reaction is entirely similar to that used in the preparation of chlorine and is expressed in the following equation:



The bromide and manganese dioxide are thoroughly mixed and are then introduced into the retort *A* (Fig. 116), the end of which just touches the water in the flask *B*. The sulfuric acid is then added. As the retort

is gently heated, the bromine is liberated, distills over, and collects under the water in the flask. The latter is kept cool by immersion in ice water in the beaker *C*.

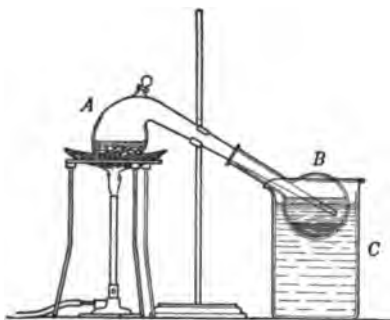
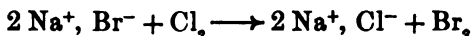


FIG. 116

In addition to the general methods applicable alike to the preparation of chlorine and bromine, an additional method may be used for the preparation of bromine. This method is based upon the fact

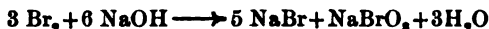
that chlorine readily liberates bromine from its compounds with the metals:



**2. Commercial method.** In the United States the entire supply of bromine comes from the salt waters obtained by sinking deep wells in two localities, namely, in the vicinity of Midland, Michigan, and in the Ohio River valley. The Michigan waters are the richer in bromine, although they only contain from 0.12 to 0.14 per cent of bromine (in the form of bromides). At Midland the bromine is liberated by electrolysis directly from the water as it comes from the wells.

**Industrial process.** The details of the process are as follows: The bromine is set free by the electric current along with some chlorine; the latter, however, reacts with the bromides to liberate bromine as described above. The amount of bromine present is so small that it remains in solution when liberated. It is blown out by a current of air and is absorbed

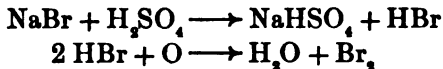
in a solution of sodium hydroxide, forming sodium bromide and sodium bromate ( $\text{NaBrO}_3$ ) in accordance with the following equation :



By heating the resulting mixture (known as *mining salts*), the sodium bromate is decomposed into sodium bromide and oxygen, just as potassium chlorate is decomposed into potassium chloride and oxygen, in the laboratory method for preparing oxygen. The bromine is thus all obtained in the form of bromides, in which form it is generally used. If the free bromine is desired, it can be obtained from mining salts by treatment with sulfuric acid.



In the Ohio River valley the bromine is obtained from the mother liquor resulting from the removal of salt by treating it with sulfuric acid and sodium chlorate. The acid reacts with the bromides, liberating hydrobromic acid, which is oxidized to free bromine by the oxygen from the sodium chlorate. The equations for the reactions are as follows :



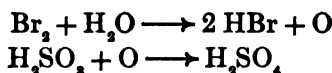
In Europe the bromine is obtained chiefly from the mother liquors left in the process of separating certain salts occurring in the Stassfurt deposits (see Stassfurt deposits). The process used in liberating the bromine from these liquors is the same in principle as that given above.

The annual production of bromine in the United States amounts to approximately 1,500,000 lb., about two thirds of which is produced at Midland and the remaining one third in the Ohio River valley.

**Bromine in the World War.** Among the poison gases used in the war were certain compounds known as *lachrymators*, because they caused inflammation of the eyes and a copious flow of tears. Bromine is the essential constituent of the most effective of these lachrymators. To obtain the supplies of bromine necessary for their production the United States during the war sunk 16 wells in the vicinity of Midland. These wells represent a total possible output of bromine amounting to about 500,000 lb. annually.

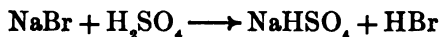
**Properties.** Bromine is a dark-red liquid whose density is 3.102. Its vapor has an offensive odor and is very irritating to the eyes and throat. The liquid boils at  $63^{\circ}$  and solidifies at  $-7.3^{\circ}$ , but even at ordinary temperatures it has a high vapor pressure, so that it evaporates rapidly, forming a reddish-brown gas very similar to nitrogen dioxide in appearance. At  $20^{\circ}$ , 100 volumes of water dissolves about 1 volume of liquid bromine, forming a solution called bromine water. Bromine is readily soluble in carbon disulfide, forming a red solution.

**Chemical conduct.** The chemical conduct of bromine is very similar to that of chlorine, except that it is less active. It combines directly with many of the same elements with which chlorine unites, but with less energy. It combines with hydrogen, and even abstracts it from some of its compounds. As would be expected, its bleaching action is much less marked than that of chlorine. Its solution in water is often used as an oxidizing agent. For example, sulfurous acid is readily converted into sulfuric acid by the addition of a suitable amount of bromine water:



**Uses.** Bromine is used principally in the preparation of bromides, which are employed to a considerable extent in photography and as medicinal agents. It is likewise used in the preparation of a number of organic drugs and dyestuffs.

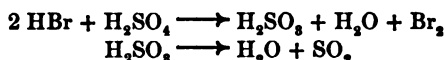
**Hydrogen bromide.** One would naturally expect that hydrogen bromide could be prepared by the same general method as that employed in the preparation of hydrogen fluoride and hydrogen chloride, namely, by the action of sulfuric acid upon a bromide such as NaBr or KBr:



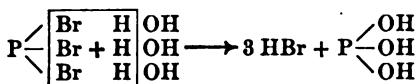
This reaction does indeed take place, the hydrogen bromide being evolved in the form of a colorless gas which fumes strongly in the air. At the same time some *bromine* is liberated,

as is indicated by the formation of a reddish vapor. The odor of sulfur dioxide can also be detected. This method, therefore, cannot be used for the preparation of pure hydrogen bromide.

This difference in the action of sulfuric acid upon fluorides and chlorides, on the one hand, and upon bromides, on the other, is due to the relatively unstable character and consequent *reducing* properties of hydrogen bromide. In the presence of concentrated sulfuric acid, which is a good oxidizing agent, a portion of the hydrogen bromide formed is decomposed, the bromine being liberated while the hydrogen is oxidized to water. The sulfuric acid is reduced to sulfurous acid in the process:



The method usually employed in the preparation of hydrogen bromide consists in the action of water upon phosphorus tribromide. The latter compound is a colorless liquid formed by the union of phosphorus and bromine, and has the formula  $\text{PBr}_3$ . When brought in contact with water it undergoes complete hydrolysis, forming hydrogen bromide and phosphorous acid ( $\text{H}_3\text{PO}_3$  or  $\text{P}(\text{OH})_3$ ). This reaction is made clearer by the use of structural formulas:



**Experimental details.** The preparation is carried out as follows: Some red phosphorus is introduced into a flask *A* (Fig. 117), and sufficient water is added to cover it. The separatory funnel *B* contains the bromine. By means of the stopcock, bromine is allowed to flow drop by drop from the funnel into the flask. The bromine,

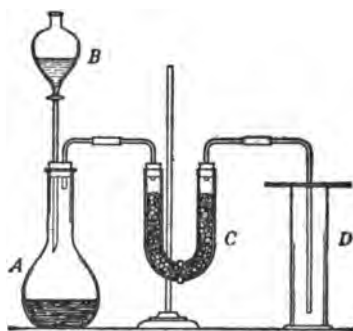
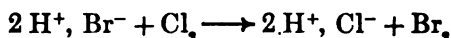


FIG. 117

on coming in contact with the phosphorus, combines with it to form phosphorus tribromide, which then reacts with water. The U-tube *C* contains glass beads which have been moistened with water and rubbed in red phosphorus. Any bromine escaping action in the flask acts upon the phosphorus in the U-tube. The hydrogen bromide is collected in *D* by displacement of air. An aqueous solution of the gas is easily prepared.

**Properties.** Hydrogen bromide very strikingly resembles hydrogen chloride in its properties. It is a colorless, strongly fuming gas and may be condensed to a colorless liquid which boils at  $-69^{\circ}$ . It is very soluble in water. Under standard conditions 1 volume of water dissolves 612 volumes of the gas. The resulting solution has a density of 1.5 and contains 88 per cent of the gas. An aqueous solution containing 48 per cent of hydrogen bromide boils at  $126^{\circ}$  and distills with unchanged concentration.

**Chemical conduct of hydrobromic acid.** Hydrogen bromide, like hydrogen chloride, has but little activity. When dissolved in water it dissociates into the ions  $H^{+}$  and  $Br^{-}$ , so that the solution is strongly acid and is known as *hydrobromic acid*. It is very similar to hydrochloric acid and reacts with metals, and with their oxides and hydroxides, forming the corresponding bromides. It differs from hydrochloric acid mainly in that it is much more easily oxidized, so that bromine is more readily liberated from it than chlorine is from hydrochloric acid. It is therefore a moderately active *reducing agent*. Free chlorine acts upon hydrobromic acid, liberating bromine, as represented in the following equation :



**Salts of hydrobromic acid; bromides.** The bromides are in general very similar to the chlorides in their properties, and are prepared by the same general methods. The bromides of the common metals are all soluble except silver bromide, mercurous bromide, and lead bromide (compare chlorides, p. 210). Silver bromide is used in photography, while sodium bromide and potassium bromide are used as medicinal agents.

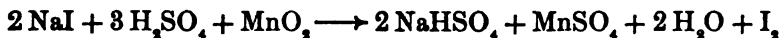
## IODINE

**History and occurrence.** Iodine is present in sea water, but in relatively small quantities. Certain seaweeds absorb the iodine from the water, thus concentrating it within their tissues. It was from the ashes obtained by burning seaweed that the French chemist Courtois, in 1812, first isolated the element,

which he termed *iodine* (from the Greek word meaning "violet-colored") because of the violet color of its vapor. Iodine is also found in certain animal life of the sea, such as sponges, oysters, and some fishes. It likewise occurs in the deposits of Chile saltpeter (sodium nitrate), and this at present constitutes the largest source of commercial iodine. It is interesting to note that small amounts of iodine exist in the human body in the thyroid gland.

**Preparation.** The principal methods used in the preparation of iodine are the following:

1. *Laboratory method.* Iodine is liberated from the iodides by the action of sulfuric acid and manganese dioxide. The reaction is similar to that which takes place in the liberation of chlorine from the chlorides, and of bromine from the bromides. The equation is as follows:



**Laboratory directions.** This method serves as a convenient one for the preparation of iodine in the laboratory. The apparatus is the same as that used in the preparation of bromine (Fig. 116, p. 358). A mixture of manganese dioxide and sodium iodide is placed in the retort *A*, sulfuric acid added, and heat applied. The iodine is evolved in the form of a violet-colored vapor which condenses to a purplish-black crystalline solid on the colder portions of the retort. By regulating the heat it can be driven over and condensed in the flask *B*, which is kept cool by ice water.

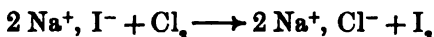
2. *Commercial method.* Commercial iodine is obtained either from seaweeds or from crude Chile saltpeter ( $\text{NaNO}_3$ ), which is known as *caliche*.

(a) *Preparation from caliche.* The iodine is distributed through the *caliche* in the form of sodium iodate ( $\text{NaIO}_3$ ) and is obtained from the mother liquor left in the purification of the nitrate. The iodine is liberated from the sodium iodate by the action of the sulfites of sodium:



The resulting iodine is removed by filtration, dried, and purified by sublimation.

(b) *Preparation from seaweeds.* Previous to the discovery of iodine in the Chile saltpeter, the element was obtained entirely from seaweeds. These weeds, known as *kelp*, were collected upon the shores of Scotland, Ireland, Japan, and France, and were dried and burned. The ashes, also known as kelp, contain a number of compounds of sodium, especially sodium carbonate and chloride, together with about 0.3 per cent of sodium iodide. The mother liquor left after the removal of the carbonate and chloride contains the sodium iodide. From this the iodine was obtained either by the action of manganese dioxide and sulfuric acid, as explained above, or by the action of chlorine:



After the discovery of iodine in Chile saltpeter, the production of the element from seaweeds practically ceased for a time, since it could be obtained from the saltpeter at a much lower cost. Later, however, the

method of recovering the element from seaweeds has been improved, so that a limited amount is again obtained from this source. The supply of iodine is greater than the demand, and new uses for the element are being sought.

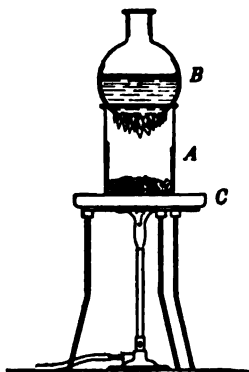


FIG. 118

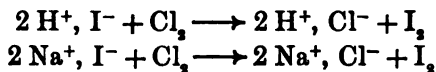
**Purification of iodine.** Iodine can be purified very conveniently in the following way: The crude iodine, mixed intimately with a little potassium iodide, is placed in a beaker A (Fig. 118), in the top of which rests a round-bottomed flask B, containing cold water. The apparatus is placed upon a sand bath C and gently heated. The iodine rapidly evaporates and condenses again on the cold surface of the flask in shining crystals. The crude iodine often contains small amounts of free chlorine and bromine. These react with the

potassium iodide present, forming respectively potassium chloride and potassium bromide, with the corresponding evolution of iodine. In this way the iodine is separated from all nonvolatile matter.

**Properties.** Iodine is a purplish-black shining solid which, when sublimed, crystallizes in brilliant plates belonging to the rhombic system. It has a density of 4.95, melts at 113.5°, and boils at 184.4°. The element has a strong, unpleasant odor, although not

so disagreeable as that of chlorine or bromine. Even at ordinary temperatures it gives off a beautiful violet vapor, which increases in amount as heat is applied. It is only slightly soluble in water, 1 part being soluble in 3750 parts of water at 15°. It is very readily soluble in a solution of potassium iodide or of hydrogen iodide, forming a dark-brown liquid. It also dissolves in carbon disulfide, forming a violet-colored liquid. A solution of iodine and potassium iodide in alcohol is known as *tincture of iodine* and is used in medicine. When applied to the skin it produces a brown stain.

**Chemical conduct.** Iodine is similar to chlorine and bromine in its chemical properties but is less active. Both of the latter elements liberate iodine from its compounds with hydrogen or the metals:

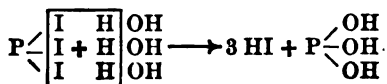


Like chlorine and bromine it combines directly with many of the metals as well as with the nonmetals. In the presence of water it acts as a mild oxidizing agent.

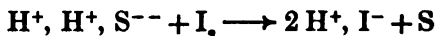
A very characteristic property of iodine is its power of imparting a blue color to a solution of starch. The reaction is a very delicate one, as can be shown by adding a few drops of an aqueous solution of iodine to a test tube containing starch solution. This property serves as a very delicate test either for free iodine or for starch.

**Uses of iodine.** Iodine is used extensively in medicine, especially in the form of tincture of iodine. It is also used in the preparation of the iodides and of certain organic dyes and drugs. The common antiseptic known as *iodoform* has the formula  $\text{CHI}_3$ .

**Hydrogen iodide.** The method generally employed for the preparation of hydrogen iodide is similar to that used for the preparation of hydrogen bromide (p. 361) and consists in the reaction between phosphorus tri-iodide and water:



The hydrogen iodide is evolved as a heavy colorless gas and may be collected by the displacement of air. An aqueous solution of the gas can be prepared by passing hydrogen sulfide into water containing finely divided iodine in suspension:



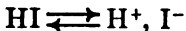
When the reaction is complete, the precipitated sulfur is removed by filtration. Solutions of the gas can be prepared in this way up to 50 per cent strength.

It will be recalled that hydrogen bromide, because of its unstable character and the consequent ease with which it is oxidized, cannot be prepared in the pure state by the action of sulfuric acid on the bromides. Since hydrogen iodide is more unstable than hydrogen bromide, it is evident that this general method is still less adapted to its preparation.

**Properties of hydrogen iodide.** Hydrogen iodide resembles hydrogen chloride and hydrogen bromide in its physical properties, being a strongly fuming colorless gas. It is 4.37 times as heavy as air. At  $0^\circ$  it is condensed to a colorless liquid by a pressure of 4 atmospheres. At  $10^\circ$  about 450 volumes of the gas dissolves in 1 volume of water. A solution containing 57 per cent of hydrogen iodide boils at  $127^\circ$  and distills with unchanged concentration. Owing to the ease with which the gas is decomposed into its elements, it acts in many respects like hydrogen, being a strong reducing agent. This might be expected from the fact that it is an endothermic compound, as shown in the equation



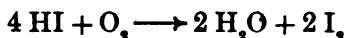
In an atmosphere of oxygen it burns, forming water and iodine. Pure hydrogen iodide, whether in the form of a gas or of a liquid, is neutral. When dissolved in water it ionizes as follows:



This solution has strong acid properties due to the hydrogen ions present, and is known as *hydriodic acid*.

**Chemical conduct of hydriodic acid.** Hydriodic acid differs from hydrochloric and hydrobromic acid mainly in the ease with

which it is oxidized. The freshly prepared solution is colorless, but soon turns brown, owing to the liberation of iodine by the oxygen of the air:



As the action continues, the iodine separates in crystalline form. The acid, as well as hydrogen iodide, is therefore a strong reducing agent. It reacts with many of the metals, as well as with their oxides and hydroxides, forming the corresponding salts.

**Salts of hydriodic acid; iodides.** These compounds are similar to the corresponding chlorides and bromides but are not so stable toward heat. They are all solids and, with the exception of the iodides of silver, mercury, and lead, the iodides of the well-known metals are soluble in water. Silver iodide is used in photography and potassium iodide in medicine.

#### QUESTIONS

1. How does the method used in the preparation of hydrofluoric acid compare with the method used for preparing hydrochloric and nitric acids? Why not use the same method for preparing hydrobromic and hydriodic acids?

2. Why is the formula for hydrogen fluoride written  $\text{H}_2\text{F}_2$ , while that for hydrogen chloride is written  $\text{HCl}$ ?

3. What is the advantage of the electrolytic method for the preparation of bromine?

4. Distinguish in properties between the liquid known as hydrogen bromide and that known as hydrobromic acid.

5. Contrast in a general way the properties of the fluorides, chlorides, bromides, and iodides.

6. What gas has been discussed that resembles the vapor of bromine in color? How could you distinguish between the two?

7. The sodium salts of hydrofluoric acid, hydrochloric acid, hydrobromic acid, and hydriodic acid are all white crystalline solids. How could you distinguish between them?

8. Zinc dissolves in each of the following acids: (a) hydrochloric acid, (b) nitric acid, (c) concentrated sulfuric acid, (d) dilute sulfuric acid, and (e) aqua regia. What are the products of the reaction in each case?

9. Chlorine forms with phosphorus a compound similar in composition and properties to that formed by bromine or by iodine. Write the equation for the reaction that would take place when this compound is brought into contact with water.

10. Suggest a method for preparing sodium bromide from sodium chloride; potassium iodide from potassium nitrate.

### PROBLEMS

1. Calculate the weight of raw material necessary for the manufacture of 100 kg. of 50 per cent hydrofluoric acid (that is, hydrofluoric acid containing 50 per cent of hydrogen fluoride).

2. If a certain salt water has a density of 1.22 and contains 0.12 per cent of bromine, what volume of this water would be required in the preparation of 10 kg. of bromine?

3. Calculate the weights of raw materials required for the preparation of 20 l. of a saturated solution of hydrogen bromide under standard conditions.

4. Calculate the weight of raw materials necessary for the preparation of 10 kg. of a solution of hydrogen iodide of constant boiling point.

5. The standard dilute hydrobromic acid of the druggist must contain not less than 9.5 per cent nor more than 10.5 per cent of HBr. 10 g. of a sample of a certain dilute hydrobromic acid solution required 12 cc. of a normal solution of potassium hydroxide to neutralize it. Is the sample standard?

## CHAPTER XXII

### THE OXYGEN COMPOUNDS OF THE HALOGENS

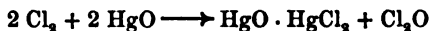
**General.** While neither chlorine nor iodine combines with oxygen directly, nevertheless a number of oxides of these two elements have been prepared by indirect methods, as described below. Fluorine and bromine, on the other hand, do not form oxides. With the exception of fluorine, the halogens form oxygen acids. The salts of some of these acids are of considerable importance.

**The oxides and oxygen acids of chlorine.** The following table includes the names and formulas of the oxides and oxygen acids of chlorine, and also shows their relation to each other:

OXIDES	ACIDS
$\text{Cl}_2\text{O}$ { chlorine monoxide (anhydride of hypochlorous acid) }	$\left\{ \begin{array}{l} \text{H}_2\text{O} + \text{Cl}_2\text{O} \longrightarrow 2 \text{HClO}, \\ \text{hypochlorous acid} \end{array} \right.$
$\text{Cl}_2\text{O}_3$ { chlorine trioxide (unknown) (anhydride of chlorous acid) }	$\left\{ \begin{array}{l} \text{H}_2\text{O} + \text{Cl}_2\text{O}_3 \longrightarrow 2 \text{HClO}_2, \\ \text{chlorous acid} \end{array} \right.$
$\text{Cl}_2\text{O}_5$ { chlorine pentoxide (unknown) (anhydride of chloric acid) }	$\left\{ \begin{array}{l} \text{H}_2\text{O} + \text{Cl}_2\text{O}_5 \longrightarrow 2 \text{HClO}_3, \\ \text{chloric acid} \end{array} \right.$
$\text{Cl}_2\text{O}_7$ { chlorine heptoxide (anhydride of perchloric acid) }	$\left\{ \begin{array}{l} \text{H}_2\text{O} + \text{Cl}_2\text{O}_7 \longrightarrow 2 \text{HClO}_4, \\ \text{perchloric acid} \end{array} \right.$
$\text{ClO}_2$ chlorine dioxide (peroxide)	

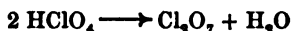
**The oxides of chlorine.** The three known oxides of chlorine, namely,  $\text{Cl}_2\text{O}$ ,  $\text{Cl}_2\text{O}_3$ , and  $\text{ClO}_2$ , are all unstable compounds. A brief discussion of each follows:

1. *Chlorine monoxide (hypochlorous anhydride) ( $\text{Cl}_2\text{O}$ ).* This compound is prepared by passing chlorine through a tube containing mercuric oxide:



It is a highly explosive yellow gas, which condenses to a liquid at  $5^\circ$ . With water it forms hypochlorous acid.

2. *Chlorine heptoxide (perchloric anhydride) ( $\text{Cl}_2\text{O}_7$ )*. This oxide is formed by the action of a strong dehydrating agent, such as phosphorus pentoxide ( $\text{P}_2\text{O}_5$ ), on perchloric acid:



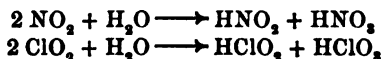
It is a colorless oily liquid and explodes with great violence when brought into contact with easily oxidizable material or when struck. With water it forms perchloric acid.

3. *Chlorine dioxide ( $\text{ClO}_2$ )*. This oxide results from the decomposition of chloric acid, as is represented in the following equation:



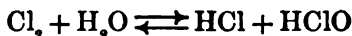
It is prepared by the action of sulfuric acid upon potassium chlorate. Chloric acid is first formed, but immediately decomposes according to the above equation. The reaction must be carried out with great care; otherwise the decomposition may take place with explosive violence. The intensity of the reaction may be shown by touching a small crystal of potassium chlorate with a glass rod moistened with concentrated sulfuric acid.

Chlorine dioxide is a yellow gas which may be condensed to a liquid boiling at  $10^\circ$ . Just as nitrogen dioxide ( $\text{NO}_2$ ) reacts with water to form a mixture of nitrous and nitric acids, so chlorine dioxide, under the same conditions, forms a mixture of chlorous and chloric acids. The similarity between the two reactions is shown in the following equations:



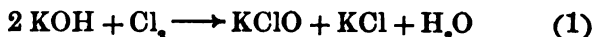
**Hypochlorous acid and the hypochlorites.** Both free hypochlorous acid and its salts (namely, the hypochlorites), are unstable and have been obtained in dilute solution only.

1. *Preparation.* Hypochlorous acid forms as a product of an equilibrium reaction when chlorine is dissolved in water:



In this case it is mixed with hydrochloric acid and easily decomposes in sunlight (p. 197). In pure form it can most readily be obtained from its salts. Solutions of the hypochlorites of sodium, potassium, and calcium are formed, along with their chlorides, by passing chlorine into *cold* solutions of their

respective hydroxides. Thus, with potassium hydroxide the reaction is expressed by the following equation:



From the resulting hypochlorites a solution of hypochlorous acid can be prepared by adding just sufficient dilute sulfuric acid to react with the hypochlorite, as expressed in the following equation:



On distilling the resulting mixture, a solution of hypochlorous acid in water is obtained. Dilute solutions of hypochlorous acid can also be obtained by the action of chlorine monoxide upon water.

**2. Properties.** Both hypochlorous acid and the hypochlorites are excellent oxidizing agents. In the presence of a substance that will combine with the oxygen formed, they decompose as follows:



On the other hand, when their solutions are heated, hypochlorous acid and its salts form chloric acid and chlorates respectively:



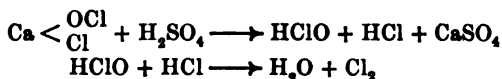
It is evident, therefore, that if one wishes to prepare hypochlorites, *the solutions must be kept cold*; otherwise chlorates are obtained.

**Uses.** The hypochlorites, as well as the free acid, are used as oxidizing agents, especially in bleaching (p. 198).

**Bleaching powder ( $\text{CaOCl}_2$ ).** When chlorine is passed into a cold solution of calcium hydroxide, there is formed a mixture of the chloride and hypochlorite of calcium (see equation (1) above); if passed over the *dry* calcium hydroxide, however, there is formed a white solid compound known commercially as *bleaching powder*, or *chloride of lime*:



The reactions of this compound are best explained on the assumption that it has the structural formula  $\text{Ca} < \begin{smallmatrix} \text{OCl} \\ \text{Cl} \end{smallmatrix}$ . In accordance with this formula it must be regarded as a *mixed salt*, namely, a calcium salt of hypochlorous and hydrochloric acids, being formed by the displacement of one atom of hydrogen in a molecule of each of these acids by a bivalent calcium atom. When an acid such as sulfuric is added to bleaching powder, free hypochlorous and hydrochloric acids are liberated and react with each other to form water and chlorine:



When bleaching powder is exposed to air, hypochlorous acid is liberated through the action of moisture and carbon dioxide.

**Manufacture and uses of bleaching powder.** Bleaching powder is made in large quantities by passing chlorine into large rooms at *A* (Fig. 119), over the floors of which is spread a layer of calcium hydroxide. The excess of

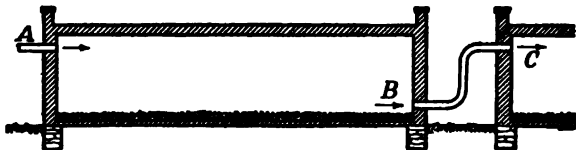
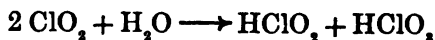


FIG. 119

chlorine leaves the room at *B* and enters a similar room at *C*. The resulting product is used commercially as a source of chlorine, since it is easily prepared and transported and the chlorine present can be liberated as desired. The commercial product generally contains from 35 to 37 per cent of available chlorine. It readily loses chlorine, however, especially at summer temperatures. It is stored and shipped in air-tight packages or iron drums, to prevent decomposition from contact with air.

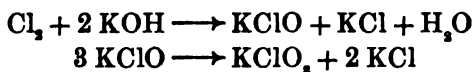
**Chlorous acid and the chlorites.** Chlorous acid is formed in small quantities when chlorine dioxide is dissolved in water:



If this solution is neutralized with potassium hydroxide, a mixture of potassium chlorite and potassium chlorate results.

The chlorites of a few of the other metals are known, but they are all very unstable.

**Chloric acid and the chlorates.** The chlorates of the metals that form soluble hydroxides are prepared by passing chlorine into hot solutions of their respective hydroxides, as already explained (p. 371). With potassium hydroxide the reactions are expressed by the following equations:

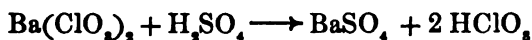


By combining the two equations the following is obtained:



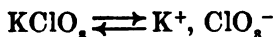
When the resulting solution is evaporated, the potassium chlorate, being much less soluble than the potassium chloride, separates first, and by repeated crystallization can be obtained in a pure state.

From the chlorates, chloric acid itself can be prepared. The most convenient method consists in adding sulfuric acid to an aqueous solution of barium chlorate:



The barium sulfate, being insoluble, separates as a white precipitate, which is removed by filtration, leaving a solution of chloric acid. This may be concentrated until it contains 40 per cent of acid. Further concentration leads to the decomposition of the acid, forming perchloric acid, water, and chlorine dioxide. The concentrated aqueous solution of the acid is a colorless liquid and has powerful oxidizing properties.

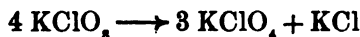
The chlorates can readily be obtained in the pure state. They are all soluble in water and ionize as follows:



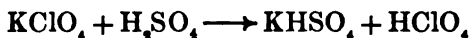
Potassium chlorate is perhaps the most important of these salts, being used in the preparation of oxygen and as an oxidizing agent.

**Preparation of hypochlorites and chlorates by electrolytic methods.** It will be recalled that the electrolysis of a solution of potassium chloride or of sodium chloride results in the formation of chlorine, together with the corresponding hydroxide of the metal. It is possible to so regulate this process that the chlorine, instead of being evolved, is retained in the solution, together with the hydroxide, with which it interacts to form hypochlorite or chlorate, according to the equations given above. This method is now coming into general use for the preparation of these salts. It is possible to obtain either the hypochlorite or the chlorate by properly choosing the conditions of the electrolysis.

**Perchloric acid and the perchlorates.** When potassium chlorate is heated, a portion of the compound changes into the perchlorate:



This reaction serves as a convenient method for preparing perchlorates, and perchloric acid itself can be obtained from these by the addition of sulfuric acid:



The perchloric acid formed is separated by distillation. This process, however, cannot be carried on under atmospheric pressure, since the temperature required decomposes the acid. Under greatly diminished pressure the boiling point of the acid is lowered to such an extent that the compound may be distilled without decomposition.

To distill a liquid under less than atmospheric pressure, the apparatus represented in Fig. 120 may be used. The liquid is placed in the distilling flask *A*, the delivery tube of which is connected with the condenser *B*. This is in turn connected by a rubber stopper with the strong receiving flask *C*, the neck of which is provided with a side tube *D*, which is attached to an air pump. A manometer *E*, for indicating the pressure, may be inserted between the receiving flask and the air pump. After exhausting the air in the apparatus to the desired extent, the liquid in *A* is gently heated and distilled over into *C*.

Pure perchloric acid is a colorless liquid. It is unstable, sometimes decomposing spontaneously with great violence. Like the other oxygen acids of chlorine, it is an excellent oxidizing agent. A concentrated solution of perchloric acid is now an article of

commerce and finds a number of applications in analytical chemistry. The perchlorates can be obtained in the pure state and are the most stable of all the salts of the oxygen acids of chlorine. They are soluble in water, forming the ion  $\text{ClO}_4^-$ , together with the metal ion. When heated to high temperatures they decompose into oxygen and the corresponding metal chlorides.

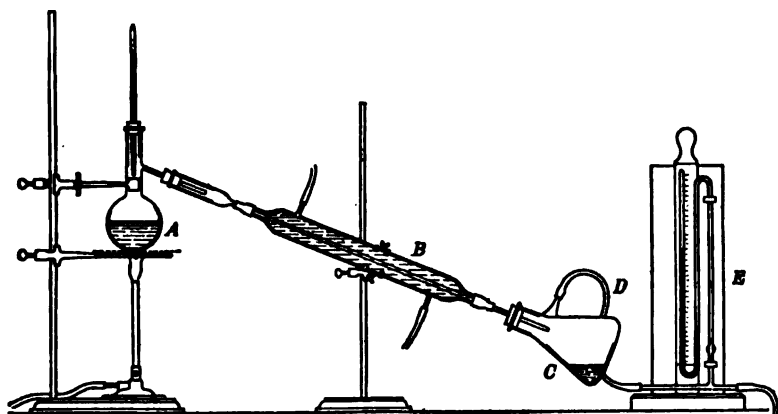


FIG. 120

To Air Pump

**The oxygen acids of bromine and their salts.** No oxides of bromine are known with certainty. The following oxygen acids have been prepared in dilute solutions: hypobromous acid ( $\text{HBrO}$ ), bromous acid ( $\text{HBrO}_2$ ), bromic acid ( $\text{HBrO}_3$ ). The hypobromites and bromates are very similar to the corresponding chlorine compounds and are prepared by the same general methods. From these salts the free acids can be prepared, as in the case of the corresponding chlorine compounds. The hypobromites are sometimes used as oxidizing agents, decomposing into oxygen and the corresponding bromide.

**Iodine pentoxide ( $\text{I}_2\text{O}_5$ ).** This is a white solid formed by heating iodic acid to  $200^\circ$ :

$$2 \text{HIO}_3 \rightleftharpoons \text{H}_2\text{O} + \text{I}_2\text{O}_5$$

The reaction is reversible, the oxide combining with water at ordinary temperatures to form iodic acid; hence the oxide may be regarded as the anhydride of iodic acid. At high temperatures it is decomposed into its constituent elements and reacts therefore as an oxidizing agent.

**Iodic acid ( $\text{HIO}_3$ ).** This acid is formed by the action of sulfuric acid upon the iodates, although it is more convenient to prepare it by oxidizing iodine directly with nitric acid. It forms white crystals and is a strong oxidizing agent.

**Hypoiodites and iodates.** These compounds are similar to the corresponding chlorine compounds in their properties and are prepared by the same general methods. Sodium iodate is found in Chile saltpeter.

**Periodic acid and the periodates.** The acid known as *periodic acid* has the formula  $\text{H}_5\text{IO}_6$ . Its salts, namely the periodates, may be prepared by the oxidation of the iodates. The one most readily obtained is an acid salt and has the formula  $\text{Na}_2\text{H}_3\text{IO}_6$ . Periodic acid itself, in the form of a white solid, can be prepared from this. When heated it decomposes, forming water, oxygen, and iodine pentoxide.

### QUESTIONS

1. In the preparation of oxygen from potassium chlorate two distinct reactions take place. Write the equation for each.
2. Chlorine, bromine, and iodine all react with alkalies such as KOH in the same general way. Write the formulas and names of all the compounds of potassium that could be formed by this general method.
3. Define the term *acid anhydride*. Enumerate the anhydrides that have been discussed.
4. What common property would you expect the oxides and the oxygen acids of the halogens to possess?

### PROBLEMS

1. If bleaching powder has the composition  $\text{CaOCl}_2 + \text{H}_2\text{O}$ , what per cent of chlorine does it contain? Contrast the result with the amount actually present in the commercial product.
2. A certain firm produces on an average 60 tons of bleaching powder daily. Calculate the weights of raw materials, NaCl and  $\text{Ca}(\text{OH})_2$ , required daily.
3. What weight of sodium chloride is necessary for the preparation of 100 kg. of sodium chlorate?
4. If you wished to use chlorine in an industry and either the free chlorine or bleaching powder served your purposes equally well, would you purchase free chlorine at 8 cents per pound or bleaching powder at 4 cents?

## CHAPTER XXIII

### SOME COMPOUNDS OF CARBON

**Introduction.** The compounds of carbon are more numerous by far than are the compounds of any other element. Nearly 200,000 of them have been described, and additional ones are being continually added to the list. The existence of such a large number of compounds is due to the property which the carbon atoms possess of combining with each other and thus building up compounds more or less complex in character. Because of their large number and also because of certain well-defined characteristics which these compounds possess, it has been found convenient to include them in a separate course of study, which is known as the chemistry of the compounds of carbon, or, more commonly, as *organic chemistry*.

**Historical.** The selection of the term *organic chemistry* dates back to an early period, when it included simply those compounds of carbon found in living organisms. It was supposed that these compounds could be formed only through the influence of the living or vital force of the organisms, and that it would be impossible to prepare them in the laboratory by synthetic methods. In 1828 the German chemist Wöhler in the course of some experiments chanced to prepare a white crystalline compound which, much to his surprise, proved to be urea, a typical organic compound. The laboratory synthesis of other compounds found in living organisms followed, until at the present time many such compounds have been made. As a result of these discoveries chemists have had to give up the old belief which led to the selection of the term *organic chemistry*. The term, however, has been retained as a convenient one for designating the chemistry of all carbon compounds. This includes most of the compounds present in organisms, these being, however, a relatively small percentage of the total number of carbon compounds known. It is not advisable for us to study any large number of these compounds at present. Only a few of the more important ones will be described.

## THE OXIDES OF CARBON AND CARBONIC ACID

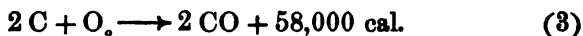
Carbon forms three well-established oxides: carbon monoxide (CO), carbon dioxide (CO<sub>2</sub>), carbon suboxide (C<sub>3</sub>O<sub>2</sub>). They are all colorless gases. But little is known of the suboxide, and no further mention will be made of it. Carbon dioxide has been described in connection with carbon, and its discussion should be reviewed at this time.

**Carbon monoxide (CO).** Carbon monoxide occurs in the gases issuing from volcanoes. It is formed in different metallurgical processes and especially when carbonaceous material such as coke and charcoal is heated in a limited supply of air. It can be prepared in a number of different ways, the most important of which are the following:

1. *By passing oxygen over hot carbon.* When oxygen is passed over carbon heated to its kindling temperature, carbon dioxide is first formed:  $C + O_2 \rightarrow CO_2 + 97,000 \text{ cal.}$  (1)

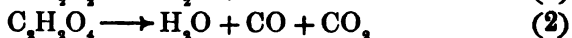
If the carbon is in great excess (or, in other words, if the supply of oxygen is insufficient for complete combustion), then the carbon dioxide at first formed is reduced to carbon monoxide by the hot carbon:  $C + CO_2 \rightarrow 2 CO - 39,000 \text{ cal.}$  (2)

Combining equations (1) and (2) we have



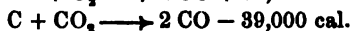
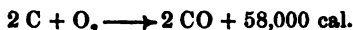
The above reactions take place when hard coal burns in a stove. When the air first comes in contact with the hot coal, carbon dioxide is formed, but as this gas rises through the glowing coal it is reduced to the monoxide, which burns with a blue flame on the top of the coal where it comes in contact with more air. If the supply of air is limited, then carbon monoxide passes off as one of the products of combustion.

2. *By the decomposition of formic or oxalic acids.* In the laboratory, carbon monoxide is usually prepared either by heating formic acid (CH<sub>2</sub>O<sub>2</sub>) or its sodium salt (equation (1) below), or by heating oxalic acid (C<sub>2</sub>H<sub>2</sub>O<sub>4</sub>) (equation (2)):



The decomposition takes place more smoothly in the presence of sulfuric acid, which assists by absorbing the water generated in the reaction. When oxalic acid is used, the resulting mixture of the gases is passed through a solution of sodium hydroxide, which removes the carbon dioxide. The carbon monoxide is then collected over water.

**Commercial manufacture of pure carbon monoxide.** During the World War large quantities of pure carbon monoxide were required for the manufacture of the poison gas known as *phosgene*. Pure oxygen cannot be used to advantage in the preparation of the monoxide on a very large scale, since the heat evolved is so great as to cause serious trouble. To overcome this difficulty, a mixture of oxygen and carbon dioxide was used in place of pure oxygen. Both of these gases react with hot carbon to form carbon monoxide:



It will be seen from the above equations that the one reaction is exothermic, while the other is endothermic. By mixing the two gases in the right proportion, therefore, the temperature of the furnace in which the reactions are carried out can be kept at any desired point.

**Properties.** Carbon monoxide is a colorless, practically odorless gas. It is 0.967 times as heavy as air and is so difficult to liquefy that it was formerly regarded as one of the permanent gases. Its critical temperature is about  $-141^\circ$  and its critical pressure 36 atmospheres. It is almost insoluble in water, but is absorbed by a solution of cuprous chloride containing either hydrochloric acid or ammonia. It is a very active compound, combining directly with a great many substances. It has a marked affinity for oxygen and burns with a blue flame:



It is therefore a strong reducing agent. For example, when it is passed over copper oxide heated in a tube, the copper is reduced to the metallic state:



Carbon monoxide also combines with chlorine, sulfur, and some of the metals, such as nickel and iron. It is very poisonous

when inhaled. Deaths not infrequently result from the stoppage of stovepipes or chimneys. The draft of air is diminished by the stoppage to such an extent that carbon monoxide rather than the dioxide forms, and not having egress through the chimney it escapes into the room. It is a very treacherous poison, since it is practically odorless and gives no warning of its presence.

**The reducing power of carbon monoxide.** Fig. 121 illustrates a method of showing the reducing power of carbon monoxide. The gas is generated by gently heating a mixture of oxalic acid and sulfuric acid in the flask *A*. The bottle *B* contains a solution of sodium hydroxide, which removes the

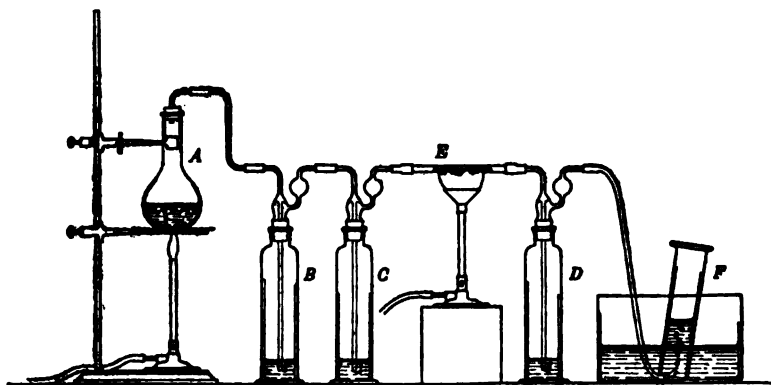


FIG. 121

carbon dioxide formed along with the monoxide. *C* contains a solution of calcium hydroxide, which serves to show that all the carbon dioxide has been removed, since its presence in the gas would cause a precipitate of calcium carbonate. *E* is a hard-glass tube containing copper oxide, which is heated by a burner. The black copper oxide is reduced to reddish metallic copper by the carbon monoxide, which is thereby changed to carbon dioxide. The presence of the carbon dioxide is shown by the precipitate in the calcium hydroxide solution in *D*. Any unchanged carbon monoxide is collected over water in *F*. If formic acid is used in place of oxalic acid, then bottle *B* is unnecessary.

**Absorbent for carbon monoxide.** During the World War extensive experiments were carried on to find some practical absorbent that could be used in gas masks to protect the wearer against the poisonous effects of carbon monoxide. Such absorbents were needed especially by gunners

on battleships, since large amounts of carbon monoxide are generated by the explosives in the firing of the big guns. The best absorbent found consists of a mixture of the oxides of manganese, copper, cobalt, and silver, and is known commercially as *hopcalite*.

**Structural formulas of the oxides of carbon.** The structural formulas of carbon dioxide and carbon monoxide are as follows:



It will be noted that in carbon dioxide the carbon is quadrivalent, while in carbon monoxide it is only bivalent. In the formation of its compounds carbon is normally quadrivalent. In the relatively few known instances in which it has a lower valence, as in carbon monoxide, the compound shows a marked tendency to combine with a bivalent group or element or two univalent groups or elements, the carbon thus passing to the normal quadrivalent condition. Those compounds, therefore, in which the carbon has a valence of less than 4 are always very reactive.

**Carbonic acid ( $\text{H}_2\text{CO}_3$ ).** This acid is unstable and is known only in the form of a very dilute solution. This solution is most readily prepared by passing carbon dioxide into water:

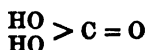


The volume of carbon dioxide absorbed in pure water is relatively small. If, however, the water contains a base, such as sodium hydroxide, in solution, the carbonic acid formed according to equation (1) reacts with the base to form the corresponding carbonate:



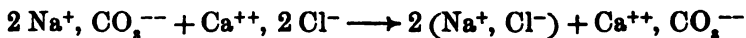
The removal of the carbonic acid results in the union of more carbon dioxide and water, according to equation (1), so that the absorption of carbon dioxide will continue until practically all the base has been changed into the corresponding carbonate.

The following structural formula is in best accord with the conduct of carbonic acid:

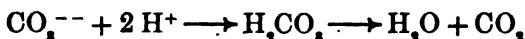


**Salts of carbonic acid; the carbonates.** Since carbonic acid is a dibasic acid, it forms both normal and acid salts.

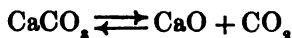
1. *Normal carbonate.* The normal carbonates are found in large quantities in nature and are often used in chemical processes. Some of these are well-known compounds. Thus ordinary *limestone* is a more or less impure form of calcium carbonate. *Marble* is nearly pure calcium carbonate in crystalline condition. Normal sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) is the well-known *soda ash*, so largely used in the manufacture of soap and glass. Among the normal carbonates only those of sodium, potassium, and ammonium are soluble in water, and these can be prepared by passing carbon dioxide into solutions of the base, as previously explained. The insoluble carbonates can be prepared by the general method for preparing insoluble compounds. Thus calcium carbonate is formed when a solution of sodium carbonate is added to a solution of any compound of calcium, such as calcium chloride:



Since carbonic acid is such a weak acid (so little ionized) and so readily decomposed, almost any acid will act upon its salts with corresponding evolution of carbon dioxide:

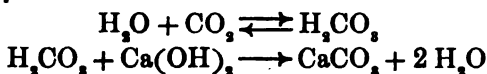


This reaction is used as a test for carbonates, since the carbon dioxide evolved can readily be detected. Most of the carbonates are decomposed by heat. Ordinary lime ( $\text{CaO}$ ), for example, is made by strongly heating calcium carbonate:



2. *Acid carbonates.* The acid carbonates are made by treating a normal carbonate with an excess of carbonic acid. The most familiar of these is sodium acid carbonate ( $\text{NaHCO}_3$ ), or ordinary baking soda. With few exceptions they are very unstable and, when heated, readily decompose even in solution. The preparation and properties of the acid carbonates may be illustrated

by a single example. If carbon dioxide is passed into a solution of calcium hydroxide (*limewater*), calcium carbonate at first precipitates:



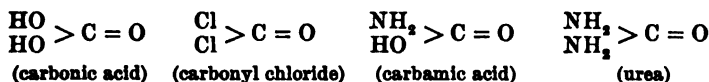
If the current of carbon dioxide is continued, however, the precipitated calcium carbonate soon dissolves. This is due to the formation of calcium hydrogen carbonate, which, being soluble, dissolves in the water present:



If now the solution is heated, the acid carbonate decomposes, and calcium carbonate once more precipitates:



**Some simple derivatives of carbonic acid.** The structural relation of carbonic acid to three of its important derivatives can be seen by comparing their structural formulas:

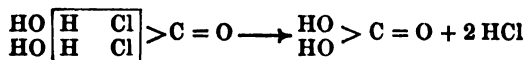


In carbonyl chloride each of the hydroxyl groups of carbonic acid has been displaced by chlorine, while in carbamic acid one hydroxyl group, and in urea both hydroxyl groups, have been displaced by the amido group  $\text{NH}_2$ .

**Carbonyl chloride (phosgene) ( $\text{COCl}_2$ ).** When a mixture of carbon monoxide and chlorine is exposed to the sunlight, the two gases combine, forming *carbonyl chloride*. This compound is commonly called *phosgene*, a word which means "generated by light," referring to the method of preparation. A more convenient as well as more efficient method of preparation consists in passing a mixture of carbon monoxide and chlorine over a form of porous charcoal which acts as a catalytic agent. Under these conditions the two gases combine with evolution of considerable heat:



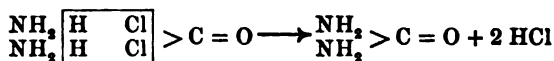
Phosgene is a colorless gas, easily condensed to a liquid boiling at 8°. With water, it forms carbonic and hydrochloric acids:



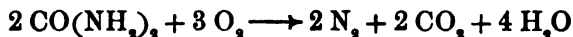
Phosgene is an important reagent in the manufacture of certain dyes. Previous to the World War, it was made in Germany for this purpose, and the small amount used in the United States was imported. After the introduction of poisonous gases as a weapon of warfare, it was found that phosgene was one of the most efficient of all known gases for this purpose, and large quantities were prepared by the warring nations. The United States led all others in the production of the gas. At the time of the signing of the armistice, our factories had a daily capacity of 30 tons, and work was in progress so that, had the war continued until January 1, 1919, our capacity would have been increased to 55 tons daily.

Carbonyl chloride bears to carbonic acid exactly the same relation that sulfuryl chloride bears to sulfuric acid (p. 324). They both belong to the general group known as *acid chlorides*.

**Urea** ( $\text{CO}(\text{NH}_2)_2$ ). Urea is formed by the action of carbonyl chloride upon ammonia:



It is a white crystalline solid, very soluble in water. Most of the waste nitrogenous matter in the human body is eliminated in the liquid excretions in the form of urea. Oxidizing agents convert it into water, carbon dioxide, and nitrogen:



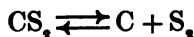
#### CARBON DISULFIDE AND THIOCARBONIC ACID

These compounds differ from carbon dioxide and carbonic acid in composition in that they contain sulfur in place of oxygen.

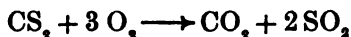
**Carbon disulfide** ( $\text{CS}_2$ ). When sulfur vapor is passed over highly heated carbon, the two elements combine, forming carbon disulfide, just as carbon and oxygen unite to form carbon dioxide. The reaction is endothermic, as expressed by the following equation:



Carbon disulfide is a heavy, colorless, highly refractive liquid which boils at  $46^{\circ}$ . When pure it has a pleasant odor, but it gradually undergoes slight decomposition and acquires a most disagreeable odor. When passed through a hot tube it decomposes:



Its vapor is very inflammable, burning in the air to form carbon dioxide and sulfur dioxide:



Carbon disulfide is a good solvent for many substances, such as gums, resins, and waxes, which are not soluble in most liquids. It is also used as an insecticide and in the manufacture of carbon tetrachloride so widely used as a fire extinguisher. Its vapor is poisonous as well as highly inflammable, so that one must exercise great care in working with it.

#### Commercial preparation of carbon disulfide.

Carbon disulfide is prepared commercially by passing sulfur vapors over hot carbon. In some factories the heat required for carrying on the reaction is generated by passing an electric current through a mixture of the raw materials in a suitable furnace. Fig. 122 represents a section of a type of furnace devised by Taylor for heating the mixture. The furnace is filled with charcoal *A*, supplied from the hopper *B* by lowering the metal cone *C*. Sulfur is admitted from the hoppers *D, D*. The wires from the dynamo lead in through the openings at *E, E*. The connections are so made that carbon rods led in through the tubes *F, F* conduct the current toward the bottom and center of the furnace. Here the heat generated is such that the carbon and sulfur combine. The resulting vapors of carbon disulfide pass up through the furnace, escaping through the tube *H*, from which they are conducted to a suitable condensing apparatus.

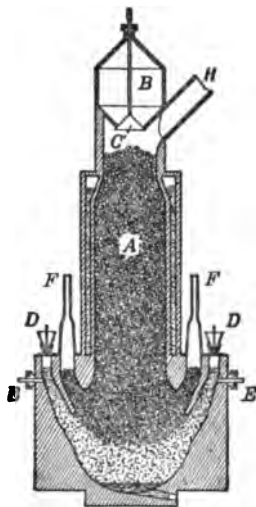


FIG. 122

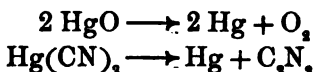
Here the heat generated is such that the carbon and sulfur combine. The resulting vapors of carbon disulfide pass up through the furnace, escaping through the tube *H*, from which they are conducted to a suitable condensing apparatus.

**Thiocarbonic acid.** Corresponding to carbonic acid and the carbonates we have thiocarbonic acid ( $\text{H}_2\text{CS}_2$ ) and the thiocarbonates such as  $\text{CaCS}_2$ . Likewise, corresponding to carbamic acid

and urea, we have thiocarbamic acid and thiourea. The reactions which these compounds undergo are in general quite similar to those of the corresponding oxygen compounds.

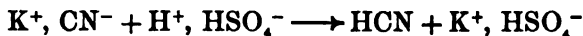
#### CYANOGEN AND SOME RELATED COMPOUNDS

**Cyanogen (CN)<sub>2</sub>.** When electric sparks are passed between carbon poles surrounded by nitrogen, some of the carbon and nitrogen unite to form a colorless gas known as cyanogen, which has the formula (CN)<sub>2</sub> or C<sub>2</sub>N<sub>2</sub>. The compound is much more readily prepared by heating mercuric cyanide (Hg(CN)<sub>2</sub>). The decomposition of the cyanide by heat is very similar to the decomposition of the oxide, as represented in the following equations:



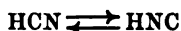
Cyanogen is a colorless gas with an odor somewhat like that of peach kernels. *It is extremely poisonous.* It burns readily, forming carbon dioxide and nitrogen. At high temperatures it combines with potassium to form potassium cyanide (KCN), which is the potassium salt of hydrocyanic acid (HCN).

**Hydrogen cyanide (HCN).** This compound, first obtained by Scheele, is well known because of its intensely poisonous properties. It can be prepared by the action of sulfuric acid upon the metallic cyanides:



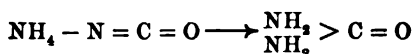
It is a light, colorless liquid boiling at 26.1°. Its odor is like that of peach kernels or oil of bitter almonds. It mixes with water in all proportions, forming the solution known as *hydrocyanic acid*, or, more commonly, as *prussic acid*. It is one of the weakest of all acids, so that its poisonous action is not due to its acid properties. Its salts are called *cyanides*. Potassium cyanide (KCN) and sodium cyanide (NaCN) are the best known. They are white solids and are extremely poisonous.

**Structural formula of hydrogen cyanide.** There has been a great deal of discussion in regard to the structural formula of hydrogen cyanide. Some of its reactions clearly indicate that the carbon present is quadrivalent and that the formula is  $\text{H} - \text{C} \equiv \text{N}$ . Other reactions indicate with equal clearness that the carbon is bivalent and that the formula is  $\text{H} - \text{N} = \text{C}$ . The conflicting evidence can best be explained upon the assumption that the substance known as hydrogen cyanide is really a mixture of both  $\text{HCN}$  and  $\text{HNC}$  in equilibrium with each other, thus



Now, if a reagent is brought in contact with this mixture which reacts only with the  $\text{HNC}$  component, then the entire mixture will act as if it were composed of the  $\text{HNC}$  component alone; for as fast as this component is withdrawn by the reacting substance, the equilibrium is overcome and more of the component is formed. Similar results follow if the reagent employed reacts only with the  $\text{HCN}$  component. Compounds that are related to each other, as  $\text{HCN}$  and  $\text{HNC}$ , each of which spontaneously changes into the other and which therefore always exist in equilibrium with each other, are known as *tautomeric compounds*.

**Cyanic acid and the cyanates.** When potassium cyanide is heated with an oxidizing agent, there is formed a white solid known as potassium cyanate,  $\text{KNCO}$ . This is the potassium salt of the unstable cyanic acid. The corresponding ammonium salt has the formula  $\text{NH}_4\text{NCO}$  or  $\text{NH}_4\text{OCN}$  (it is uncertain which is correct). When ammonium cyanate is dissolved in water and the solution is heated, urea is formed. It was by this method that Wöhler synthesized urea (p. 377). The change that takes place when ammonium cyanate is heated is represented by the following equation:



Corresponding to cyanic acid and the cyanates, we have also thiocyanic acid and the thiocyanates.

**Isomeric compounds.** It will be noted that ammonium cyanate and urea have the same molecular formula, namely,  $\text{N}_2\text{H}_4\text{CO}$ . Compounds like these, which have the same molecular formula, are known as *isomeric compounds*, or simply as *isomers*. Their

difference in properties is due to the different arrangement of the atoms in the molecule. A great many isomeric compounds are known, especially among the compounds of carbon.

### QUESTIONS

1. Name important reducing agents among the substances so far discussed.
2. The "hardness" of water is often due to the presence of calcium hydrogen carbonate. How could such waters be softened?
3. Contrast the chemical conduct of carbonic acid and sulfurous acid.
4. How could you distinguish between sodium carbonate and sodium sulfite? between carbon monoxide and nitric oxide?
5. How could you tell whether a certain rock was limestone or fluorite?
6. Distinguish clearly between isomeric, polymeric, and tautomeric compounds.
7. Is the function of the electric current the same when employed (a) for decomposing water and (b) for the manufacture of carbon disulfide?

### PROBLEMS

1. What weight of oxalic acid would be required to generate sufficient carbon monoxide to reduce 100 g. of copper oxide?
2. Contrast the volume of carbon monoxide with the volume of carbon dioxide formed by its combustion.
3. What weight of carbon dioxide must be passed into 10 l. of a normal solution of sodium hydroxide to neutralize it?
4. Calculate the amounts of carbon and chlorine required for the manufacture of 1000 kg. of phosgene.
5. What weight of carbon would be required to generate sufficient heat to change 100 kg. of water at 20° into steam at 100°?
6. What weight of carbon monoxide would be required to generate sufficient heat for the preparation of 100 kg. of carbon disulfide?

## CHAPTER XXIV

### MOLECULAR WEIGHTS

**Introduction.** It was shown in Chapter VII that from the results of the analysis of a compound it is possible to calculate a formula which correctly represents its composition. It was assumed, however, that we already possess a concordant system of atomic weights. Moreover, it was pointed out that the formula so calculated is merely the *simplest one* possible, and does not necessarily represent the real composition of the molecule. Thus the *simplest* formula for hydrogen peroxide is HO, but there is good reason for concluding that the *molecular* formula is really  $\text{H}_2\text{O}_2$ .

It is the purpose of the present chapter to develop the methods (1) by which the true molecular formulas of compounds may be determined, and (2) by which a concordant system of atomic weights may be selected.

**I. Methods for determining molecular weights.** In solving the two problems that have just been stated, it may be supposed that we must first obtain a correct system of atomic weights, and from these deduce the true molecular weights. As a matter of fact this order must be reversed, and we shall take up first the problem of arriving at the correct molecular weight of compounds.

**Methods for securing equal numbers of molecules of different compounds.** If it were possible actually to count out equal numbers of molecules of various compounds into separate piles, it is evident that the ratio between the weights of the several piles would be the same as the ratio between the weights of the individual molecules. If one of the piles were to be taken as standard, it would then be possible to state how much heavier

each kind of molecule is than those of the standard pile, and such figures would be the *relative* weights of the various molecules.

Evidently this cannot be done directly, but it has been found possible to accomplish the same results indirectly through the discovery that *certain properties of substances are dependent merely upon the number of molecules present*, quite irrespective of their character. This provides a ready means for deciding when we are dealing with the same number of molecules of different substances, and consequently for determining their relative weights. Several of these properties will now be discussed.

1. *The volume of a gas is proportional to the number of molecules which it contains.* There are many reasons for believing that this statement is true, though it is evident that its truth cannot be experimentally demonstrated. Historically its acceptance was based upon the formulation of a very important law, together with a hypothesis as to the meaning of the law.

*The law of Gay-Lussac.* In the early years of the nineteenth century the Frenchman Gay-Lussac investigated the proportion by volume in which gases combine, as well as the relation between their individual volumes and that of the product formed. His studies brought to light the remarkable relationships illustrated in the following equations:

1 vol. hydrogen + 1 vol. chlorine  $\longrightarrow$  2 vol. hydrogen chloride

2 vol. hydrogen + 1 vol. oxygen  $\longrightarrow$  2 vol. steam

3 vol. hydrogen + 1 vol. nitrogen  $\longrightarrow$  2 vol. ammonia

2 vol. carbon monoxide + 1 vol. oxygen  $\longrightarrow$  2 vol. carbon dioxide

The conclusions which he reached, verified by all subsequent research, may be stated in the following form, known as the *law of Gay-Lussac*: *When two gases combine, there is an integer ratio between their volumes, as well as between the volume of either of them and that of the product, provided it is a gas.*

*Avogadro's hypothesis.* In 1811 Avogadro, professor of physics at Turin, suggested that the most probable explanation of this striking generalization is that *equal volumes of all gases under the same physical conditions contain the same number of molecules.*

This generalization is known as *Avogadro's hypothesis*. It is in complete accord with the various gas laws, and can be shown to be a logical conclusion if we accept the kinetic theory of gases.

Assuming the truth of this hypothesis, we have at once a means of setting apart an equal number of molecules of various gases, for they will be contained in any definite volume which we may choose, for example, in 1 l. *The ratios between the weights of 1 l. of each of the various gases measured under the same conditions will be the same as those between the weights of the several kinds of molecules.*

2. *The lowering of the freezing point of a solvent is proportional to the molecular concentration of the solute.* In the chapter on solutions it was shown that the lowering of the freezing point of a solution depends not upon the *kind* of molecules dissolved in the solvent but merely upon *their concentration* in it, provided there is no ionization (law of Raoult). Conversely, when the freezing point of a given quantity of a solvent is lowered to the same extent by two different substances, we have an equal number of molecules of solute present in the two cases. If, therefore, a definite quantity of a solvent is taken, say 1 l., and experiments are made to determine the quantities of various substances which must be dissolved in it to produce a definite lowering of the freezing point, say of  $1^{\circ}$ , then these quantities will contain an equal number of molecules, and the ratio between their weights will be the same as that between the weights of the individual molecules.

3. *Change in boiling point and vapor pressure.* In an entirely similar way the boiling point and the vapor pressure of liquids have been found to be changed to the same extent by the same number of dissolved molecules, irrespective of their character, and by measurement of these changes it is possible to determine the relative weights of the molecules producing them.

**The standard of molecular weights.** Having devised methods for the determination of the relative weights of molecules, the next step is to agree upon some one substance as a standard, and then to express these weights as multiples of that of the

standard molecule. Since molecular weights are most frequently determined by measurements of the volumes of gases, it is best to select as a standard some gaseous substance, preferably an element. Various gases have been chosen at different times, the choice being guided merely by convenience. Hydrogen commends itself as being the lightest of all gaseous substances, and if it is taken as standard, all others will have weights greater than unity. On the whole, oxygen serves as the most satisfactory standard, and is now universally adopted. *We need only determine the weight of a liter of each kind of gas, and state how much heavier it is than that of a liter of oxygen, to have a series of molecular weights based on oxygen as unity.*

**Weight of oxygen taken as 32.** The assumption of oxygen as unity is open to the objection that a number of gases are lighter than oxygen, and their molecular weights would, on this basis, be less than unity, which would be undesirable. Hydrogen is the lightest of all, the ratio between equal volumes of hydrogen and oxygen being 1 : 15.87. The smallest whole number assignable to oxygen which will at the same time place hydrogen as great as unity is therefore 16.

In adopting any standard for molecular weights, however, it should be remembered that the same standard must serve for both molecules and atoms. If there should be any reason for thinking that the molecule of hydrogen consists of more than one atom, it would be better to adopt a still higher value for the oxygen molecule, so as to place the hydrogen *atom* at a value as great as unity.

That the hydrogen molecule consists of at least two atoms is shown by the following reasoning. When hydrogen combines with chlorine, the volume relations are expressed thus :



According to Avogadro's hypothesis the two volumes of hydrogen chloride must contain twice as many molecules as the one volume of either hydrogen or chlorine. But each of the

molecules of hydrogen chloride must contain at least one atom of hydrogen. This accounts for twice as many atoms of hydrogen in the hydrogen chloride as there are molecules in the one volume of hydrogen. These relations can be brought into harmony with the hypothesis of Avogadro by assuming that *each molecule of hydrogen is made up of two atoms*. It was Avogadro who first suggested that many gaseous molecules consist of two atoms.

It will be noticed that this reasoning merely shows that there are twice as many hydrogen atoms in the hydrogen molecules as there are in those of hydrogen chloride. There might be two in each of the latter and four in the former, but since there are no facts known which point to the larger numbers, we make the simplest assumption possible, and conclude that the numbers are two and one.

Since it is the atom of hydrogen rather than its molecule which we wish to hold as great as unity, and since it appears that there are two atoms in the molecule, we shall have to double the value 16, which we have provisionally adopted for the oxygen molecule, and place it at 32. This will give the value 2.016 to the hydrogen molecule and 1.008 to the hydrogen atom.

**The gram-molecular volume.** If we adopt  $O_2 = 32$  as the basis for our molecular weights, then 32 g. of oxygen will be 1 gram-molecule of oxygen. Since 1 l. of oxygen weighs 1.429 g., the volume occupied by 32 g. will be  $32 \div 1.429 = 22.38$  l., or approximately 22.4 l. But if 22.4 l. contains 1 gram-molecule of oxygen, *it will also contain 1 gram-molecule of any other gas*, for the hypothesis of Avogadro tells us that a given volume will contain an equal number of any kind of molecules. The weight of 22.4 l. of any gas will therefore give a number that will be the same as the molecular weight of the gas compared with  $O_2 = 32$  as a standard.

In this way we reach the general rule: *To determine the molecular weight of a gaseous substance, referred to oxygen = 32, find the weight of 22.4 l. of the gas under standard conditions.*

**Experimental determination of molecular weights.** In an actual experiment we determine the exact weight of any convenient volume of a gas under any convenient conditions of temperature and pressure, and from this weight calculate the weight of 22.4 l. under standard conditions. Two general methods for making such a determination are in use.

1. *Method of Dumas.* This older method for determining vapor densities, employed by Dumas as early as 1827, is readily adapted to the present purpose. A small glass bulb of about 100 cc. capacity is attached to an air

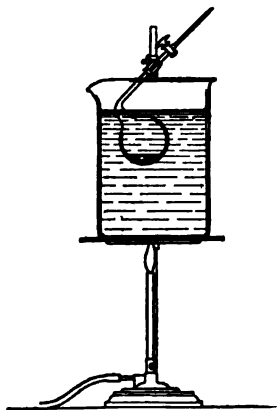


FIG. 123

pump, exhausted of the air which it contains, and weighed empty. The flask is then filled with the gas under investigation, and again weighed. If we know the volume of the flask, the weight of the gas which fills it, and the temperature and pressure under which it was filled, it is easy to calculate the weight of 22.4 l. of the gas under standard conditions. The method is also applicable to liquids that are easily vaporized. The liquid whose molecular weight is to be determined may be placed in the flask and the flask immersed in a bath, the temperature of which is above the boiling point of the liquid (Fig. 123). The liquid rapidly boils away, leaving the flask filled with the vapor of the liquid at the temperature of the bath and the pressure

of the atmosphere. The flask may then be closed and its weight determined. From the results of this experiment, together with the volume and weight of the empty flask, the molecular weight of the liquid in the vapor state may be deduced.

2. *Method of Victor Meyer.* In 1878 Victor Meyer devised a more convenient though less accurate method, which depends upon a somewhat different principle. The apparatus employed is represented in Fig. 124. The inner vessel *A* is a long, narrow tube expanded into a bulb at the lower end, open at the upper end *B*, and furnished with a slender side tube *C* near the top. This vessel is placed in an outer jacket *D*, which contains some liquid, frequently water, by boiling which the inner vessel may be raised to a definite, steady temperature. When this has been effected, a graduated collecting tube *E* is filled with water and inverted over the end of the delivery tube *C*, as shown in the figure. A small quantity of a liquid (from 0.1 to 0.2 g.) whose molecular weight is to be determined is weighed

out in a minute bottle *F*, and the bottle is dropped in at *B*, the opening being quickly closed by a stopper. The liquid in the jacket must have a boiling point higher than that of the liquid whose molecular weight is to be determined. The liquid in the bottle will then be very rapidly converted into vapor in the bulb, and an equal volume of air from the upper part of the vessel *A* will be forced over into the measuring tube *E*, which can then be measured at room temperature and calculated to standard conditions. Since all gases undergo the same volume changes when temperature and pressure are altered, it is evident that this calculation gives us the volume which the vapor of the weighed substance would occupy under standard conditions if it were possible so to obtain it. From the weight and the volume it is easy to calculate the weight of 22.4 l.

**Freezing-point method.** There are, however, many substances whose vapor density cannot be measured. In some cases the temperature of volatilization is so high that containing vessels which will stand such a temperature cannot be constructed. In other cases the substance decomposes before vaporizing, as is true with most metallic salts and a great many organic substances, such as sugar. In many of these cases it is possible to determine the molecular weight by measurements of the lowering of the freezing point of some suitable solvent. The first step is to determine the lowering produced by a gram-molecular weight of some substance whose molecular weight is known from the methods just described. For example, such methods give us the formula  $C_2H_6O$  for alcohol, with a molecular weight of 46. If 46 g. of alcohol is dissolved in a liter of water, it is found that the freezing point of the water is lowered by  $1.87^\circ$ . According to the law of Raoult (p. 185) 1 gram-molecular weight of *any* substance dissolved in 1 liter of water will lower the freezing point by the same amount (provided it is not ionized or changed

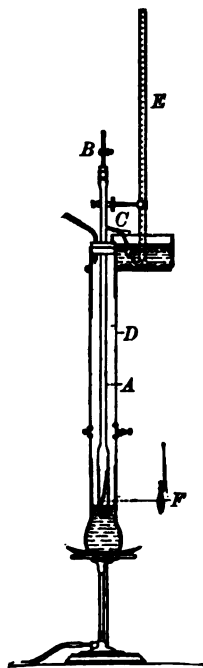


FIG. 124

chemically). It will be seen that in a general way the determination of this value of molecular lowering ( $1.87^\circ$ ) corresponds to the fixing of the gram-molecular volume for gases (22.4 l.).

To determine the molecular weight of some substance of unknown value we need only dissolve a weighed quantity in a definite volume of water and determine the lowering of the freezing point. The calculation of the molecular weight is then very simple. Thus 0.46 g. of sugar, dissolved in 20.35 g. of water, produced a lowering of  $0.126^\circ$ . The proportion

$$\begin{aligned} 20.35 : 1000 &= 0.46 : x \\ x &= 22.604 \end{aligned}$$

gives the weight which would produce the same lowering if dissolved in a liter of water. But a gram-molecular quantity would produce a lowering of  $1.87^\circ$ , so that 22.604 g. constitutes  $\frac{0.126}{1.87}$  of a gram-molecular weight of sugar. The molecular weight as determined by this experiment is therefore 335.4 (the correct weight being 342).

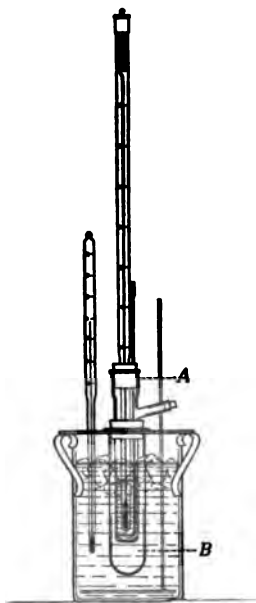


FIG. 125

**Freezing-point apparatus.** The apparatus usually employed in such measurements, known as the Beckmann apparatus, is represented in Fig. 125. The weighed solvent (water) is placed in the inner tube *A*, and the thermometer arranged to dip into the liquid. A suitable stirrer is also provided. The tube *A* is hung in a larger tube *B*, which is empty, and the latter is surrounded by a cooling mixture of ice and salt. This cools the air in *B* below the freezing point of water, and makes it possible to freeze a portion of the solution in *A*. The thermometer is of special construction, so that changes of temperature as small as  $0.001^\circ$  can be read. By noting the freezing point of the pure water, and also the freezing point after the introduction of a weighed quantity of some substance, the data for the calculation are readily obtained.

**Experimental molecular weights merely approximate.** The methods just described are all subject to many sources of slight error, so that the value for the molecular weight as determined by them usually varies from the true value by as much as from 2 to 3 per cent. The great importance of these methods lies in the fact that they give us reliable information as to what *multiple* of the formula weight is the true molecular weight — for example, whether the molecular weight of sugar is a number near 171 or near 342, and errors of several per cent in no wise impair the value of the methods.

**Calculation of formulas from molecular weights.** Having devised satisfactory methods for determining molecular weights, it is a simple matter to calculate the correct molecular formula. Thus, if analysis shows that the composition of sulfur chloride is correctly represented by the formula  $\text{SCl}$ , having a formula weight of 67.52, while measurement of its vapor density gives the value 133.2 as its approximate molecular weight, it is evident that the simple formula must be doubled to obtain the molecular formula. This gives the formula  $\text{S}_2\text{Cl}_2$ , with a molecular weight of 135.04.

**Summary.** In general the molecular formula is found by the following procedure: (1) determine the simplest formula by analysis; (2) determine the approximate molecular weight; (3) multiply the simplest formula by the integer which will give a value near to the experimentally determined molecular weight.

**II. Selection of atomic weights.** Having devised a reliable method for determining the molecular weights of *compounds*, let us now turn to the second problem proposed for this chapter, namely, the selection of the atomic weights of the *elements*.

It will be recalled that the direct analysis of compounds enables us to determine the combining weights of the elements with great precision, but it does not tell *which multiple of the simplest combining weight really represents the relative weight of the atom*. The real problem before us, therefore, is how to decide definitely what multiple of the combining weight should be chosen as the atomic weight.

**Approximate atomic weights deduced from molecular weights.** We first determine the *approximate* atomic weight as follows. In the table on the opposite page the first column gives the names of a number of compounds containing oxygen, hydrogen, carbon, nitrogen, chlorine, and sulfur. The second column gives the molecular weights of the compounds as determined by one of the methods just described, the values being subject, as a rule, to an error of several per cent. The succeeding columns show how many of the units of the molecular weight must be assigned to the several atoms composing the molecules. These values are obtained by carefully analyzing the compounds and then multiplying the molecular weights by the percentage of each element present. Thus, if the molecular weight of carbon monoxide is approximately 27, and analysis shows that the substance contains 42.96 per cent of carbon, it is clear that, of the 27 units constituting the molecular weight,  $27 \times 0.4296 = 11.6$  must be assigned to the carbon atoms present. The remaining 15.4 units ( $27 - 11.6$ ) must be the weight of the oxygen atoms.

Now each molecule must be made up of some definite number of each kind of atoms composing it, so that *in the molecular weight of the compound the part by weight assigned to each atom must represent either the relative weight of the atom or some multiple of it*. In a considerable number of compounds of a given element the molecules of some of these will, in all probability, contain but a single one of these atoms. In such compounds the part of the molecular weight assigned to the atom in question will be approximately its real atomic weight. In all other compounds containing this element the parts assigned to its atom will be some multiple of this smallest weight. An examination of the several columns in the table will show that this is the case. In each column all the values listed are approximate multiples of the smallest one, which is indicated in round numbers at the bottom of the column. These values are approximate only, for the reason that the molecular weights are not accurate; and so the values derived from them are subject to the same error.

**Summary.** For the determination of the *approximate* atomic weight of an element we therefore reach the following rule: (1) determine the molecular weight of a large number of compounds of the element in question; (2) analyze these compounds; (3) multiply the molecular weight of each by the percentage of the element present in the compound. The least value so obtained will be the *approximate* atomic weight.

TABLE ILLUSTRATING CALCULATION OF ATOMIC WEIGHTS

NAME	MOL. WEIGHT	PART O	PART H	PART C	PART N	PART Cl	PART S	FORMULA
Carbon monoxide . .	27.	15.4		11.6				CO
Carbon dioxide . .	44.4	32.2		12.2				CO <sub>2</sub>
Methane . . . . .	16.5		4.1	12.4				CH <sub>4</sub>
Acetylene . . . . .	25.8		2.2	23.6				C <sub>2</sub> H <sub>2</sub>
Benzene . . . . .	77.6		5.8	71.8				C <sub>6</sub> H <sub>6</sub>
Alcohol . . . . .	46.6	16.1	6.3	24.2				C <sub>2</sub> H <sub>5</sub> O
Sugar . . . . .	340.0	174.7	22.2	143.1				C <sub>12</sub> H <sub>22</sub> O <sub>11</sub>
Hydrogen chloride .	36.7		1.1			35.6		HCl
Carbon tetrachloride	154.0			11.9		142.1		CCl <sub>4</sub>
Chloroform . . . .	121.0		1.1	12.1		107.7		CHCl <sub>3</sub>
Sulfur chloride . .	133.2					70.1	63.1	S <sub>2</sub> Cl <sub>2</sub>
Sulfuryl chloride .	136.2	32.4				71.5	32.8	SO <sub>2</sub> Cl <sub>2</sub>
Sulfur dioxide . .	64.15	32.85					31.3	SO <sub>2</sub>
Carbon disulfide . .	76.9			12.3			64.7	CS <sub>2</sub>
Ammonia . . . . .	17.3		3.1		14.2			NH <sub>3</sub>
Nitrous oxide . . .	43.5	15.9			27.6			N <sub>2</sub> O
Nitrogen pentoxide .	107.1	79.3			27.8			N <sub>2</sub> O <sub>5</sub>
Nitric acid . . . .	63.75	48.4	1.05		14.3			HNO <sub>3</sub>
Water . . . . .	17.9	15.9	2.0					H <sub>2</sub> O
Hydrogen peroxide .	34.3	32.2	2.1					H <sub>2</sub> O <sub>2</sub>
Approximate atomic weight		16.00	1.0	12.0	14.0	35.5	32.0	

The accurate determination of atomic weights. For *exact* determinations of atomic weights we must now return to the combining weights (p. 111). These can be determined with great precision by the analysis of suitable compounds, and they are always either identical with the atomic weights or bear a simple integer relation to them. Thus, from the above table it will be

seen that the *approximate* atomic weight of sulfur is 32. The combining weight of sulfur, as determined by the analysis of sulfur dioxide, is found to be 8.015. The exact atomic weight is evidently four times the combining weight, since this will give a number approximating 32. Hence the true atomic weight of sulfur is  $4 \times 8.015$ , or 32.06.

The molecular weights of the elements. If the molecular weights of the elements themselves are determined by measurement of their vapor densities at temperatures above their boiling points, very interesting results are obtained, as is shown in the following table:

THE MOLECULAR WEIGHTS OF SOME ELEMENTS

ELEMENT	TEMPERATURE	MOLECULAR WEIGHT	FORMULA
Sodium . . . . .	Red heat	25.4	Na = 23.0
Potassium . . . . .	Red heat	37.6	K = 39.1
Zinc . . . . .	1740°	76.4	Zn = 65.37
Cadmium . . . . .	1040°	114.0	Cd = 112.4
Mercury . . . . .	448°	198.5	Hg = 200.6
Oxygen . . . . .	Up to 1690°	32.0	O <sub>2</sub> = 32.0
Nitrogen . . . . .	Up to 1690°	28.08	N <sub>2</sub> = 28.02
Hydrogen . . . . .	Up to 1690°	2.006	H <sub>2</sub> = 2.016
Chlorine . . . . .	200°	70.9	Cl <sub>2</sub> = 70.92
Iodine . . . . .	448°	254.8	I <sub>2</sub> = 253.84
Iodine . . . . .	1700°	127.0	I = 126.92
Thallium . . . . .	1730°	412.4	Tl <sub>2</sub> = 408.0
Ozone . . . . .	0°	47.9	O <sub>3</sub> = 48.0
Phosphorus . . . . .	318°	128.0	P <sub>4</sub> = 124.16
Phosphorus . . . . .	1700°	91.2	P <sub>4</sub> + P <sub>2</sub>
Sulfur . . . . .	193°	251.0	S <sub>8</sub> = 256.56
Sulfur . . . . .	1719°	63.6	S <sub>2</sub> = 64.14

From this table it appears that the metallic elements have molecular weights which are identical with their atomic weights as deduced from their compounds. This is true of all the metals whose molecular weights have been determined by vapor-density methods, with the exception of thallium. Judging by other

methods of measurement it is also true of the gases constituting Group 0 in the periodic table, all of which appear to be monatomic. Aside from these, the elements which usually occur in the gaseous state, as well as many others, have molecular weights double their atomic weights, the molecule consisting of two atoms. As the temperature is raised, many of these molecules, as with iodine, show a marked tendency to break down into single atoms, setting up a state of equilibrium between the molecule and the atoms. Ozone appears to consist of three atoms of oxygen. Phosphorus, as well as arsenic, has four atoms in the molecule at ordinary temperatures, but at high temperatures approaches a diatomic molecule. Sulfur molecules consist of eight atoms at low temperatures (measured under very small pressures), but at high temperatures these decompose into diatomic molecules. At intermediate temperatures there is equilibrium between the two forms.

**The law of Dulong and Petit.** As early as 1819 Dulong and Petit discovered a relationship between the atomic weights of solid elementary substances and their specific heats, which has been of much assistance in fixing upon the multiple of the combining weight which correctly represents the atomic weight. Their generalization was of special service at a time before it was possible to determine the vapor density at high temperatures.

These investigators found that the atomic weight multiplied by the specific heat gives an approximate constant whose value is about 6.25. This is called the *atomic heat* of the elements. By the *specific heat* is meant the quantity of heat required to raise the temperature of a gram of the solid substance one degree. Evidently the approximate atomic weight of an element will be given by the equation

$$\text{Atomic weight} = 6.25 + \text{specific heat}$$

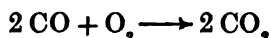
Many more recent researches have been carried out on this subject, notably by Regnault, and the following table gives some of the values accepted at the present time. In the case of some of the elements, notably boron, carbon, silicon, and glucinum, the value obtained deviates widely from the average under ordinary conditions, but approaches the normal value at high temperatures.

TABLE OF SPECIFIC HEATS

ELEMENT	ATOMIC WEIGHT	SPECIFIC HEAT	ATOMIC HEAT
Lithium . . . . .	6.94	0.941	6.53
Sodium . . . . .	23.00	0.293	6.74
Magnesium . . . . .	24.32	0.245	5.95
Aluminium . . . . .	27.1	0.214	5.80
Phosphorus . . . . .	31.04	0.202	6.26
Sulfur . . . . .	32.07	0.203	6.51
Potassium . . . . .	39.10	0.166	6.49
Iron . . . . .	55.84	0.112	6.26
Copper . . . . .	63.57	0.095	6.04
Zinc . . . . .	65.37	0.093	6.07
Silver . . . . .	107.88	0.067	6.15
Platinum . . . . .	195.2	0.0325	6.34
Gold . . . . .	197.2	0.0324	6.40
Mercury . . . . .	200.6	0.0333	6.66
Lead . . . . .	207.1	0.0315	6.52

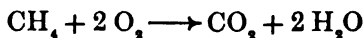
III. Some applications to chemical calculations. The relations brought out in connection with Avogadro's hypothesis may be turned to account in many calculations involving gas volumes.

1. *Volume changes in reactions.* In any reaction which involves gaseous products the volume changes may be at once noted. For example, when carbon monoxide burns, we have the equation

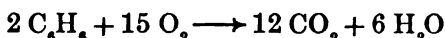


Since equal volumes contain the same number of molecules, it is evident that the converse is true; namely, when equal numbers of molecules are present the volumes are equal. The double formula weight of carbon monoxide will have the same number of molecules as the double formula weight of the dioxide, and each of these will be twice the volume of the single formula weight of oxygen. The equation may therefore be read:  $2 \times 22.4$  l. of carbon monoxide +  $22.4$  l. of oxygen produce  $2 \times 22.4$  l. of carbon dioxide.

In the combustion of marsh gas ( $\text{CH}_4$ ) we have the following equation:



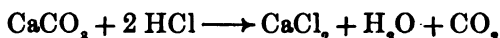
There is the same number of molecules on each side of the equation, and (supposing that the water remains as a vapor) the volumes are consequently equal. There is no change in volume on combustion. With benzene ( $C_6H_6$ ) there is a slight expansion, as is shown in the following equation :



In this case 17 volumes produce 18. If the combustion takes place under such conditions that the benzene is a liquid at the outset and the water is liquid at the conclusion of the reaction, then 15 volumes produce 12, the volumes of the two liquids being so small as to be negligible.

*Effect of temperature.* All the statements of the last paragraph presuppose that there is no change in the temperature between the measurements of volumes. As a matter of fact, all these reactions evolve much heat, and since the specific heat of gases is small, the temperature of the resulting gases is very greatly raised. If the initial measurements are made at  $0^\circ$ , each rise in temperature of  $273^\circ$  will double the volume of the gases formed, and, as the temperature may easily go as high as  $1500^\circ$ , it will be seen that there may be a momentary expansion to five or six times the calculated volume.

2. *Volume of a gas evolved from a solid.* The properties of the gram-molecular volume suggest a direct method of calculating the volume of a gas produced in a reaction without first calculating its weight. For example, take the equation



It is evident that 1 gram-molecular weight of calcium carbonate will produce 1 gram-molecular volume of carbon dioxide. Since the molecular weight of the former is, in round numbers, 100, it follows that 100 g. of the carbonate will produce 22.4 l. of the dioxide, and the same ratio will hold between any other quantities in the reaction. Thus, if it is desired to know the volume produced from 20 g., it is sufficient to note that this is

$\frac{10}{100}$  of the molecular weight, and that as a result  $\frac{10}{100}$  of the gram-molecular volume of gas will be produced; that is,  $\frac{10}{100} \times 22.4 = 4.48$  l. It will be seen that it is not necessary to know the weight of a liter of the gas in order to make such calculations.

3. *Weight of a liter of a gas.* It is often desirable to know the weight of a liter of various gases, and occasionally it is not convenient to search for the values in tables. It is always possible to obtain an *approximate* value by recalling the fact that the molecular weight in grams occupies 22.4 l. If the formula of the gas is known, it is therefore sufficient to divide the molecular weight by 22.4 in order to determine the weight of 1 l. The weight so obtained is approximate only for the reason that the gas laws are only an approximately correct statement of the conduct of gases, and consequently Avogadro's hypothesis, which is based upon these laws, is not rigidly true.

### QUESTIONS

1. What is the change in volume in the action of oxygen on nitric oxide?

2. If you dissolve 10 g. of two different solids in 100 cc. of water each and observe different lowerings of the freezing point, what conclusions may you draw as to the relative molecular weights of the two? If they are electrolytes, how will this fact modify your conclusion?

3. How many liters of oxygen will be required for the complete combustion of 6 l. of CO (both measured under the same conditions)? What volume of CO<sub>2</sub> will be formed?

4. If oxygen had been adopted as a standard for atomic and molecular weights, O = 100, what would be the gram-molecular volume of gases?

5. In the Victor Meyer method is it necessary to know the temperature to which the vapor is heated?

6. Which will occupy the greater volume, 1 g. of oxygen or 1 g. of nitrogen?

7. Compare the change in volume in the combustion of 1 l. of methane (CH<sub>4</sub>) in oxygen and in ozone.

## PROBLEMS

1. In an experiment by the method of Victor Meyer the following data were obtained: the small bulb contained 0.11 g. of chloroform; the volume of air collected over water at  $20^{\circ}$  was 22.5 cc.; the barometer read 755 mm. Calculate the molecular weight of chloroform.

2. In an experiment by the freezing-point method the following data were obtained: 2.2315 g. of cane sugar dissolved in 100 g. of water depressed the freezing point of the water  $0.122^{\circ}$ . Calculate the molecular weight of the sugar.

3. Given the data:

Specific heat of Fe = 0.112; combining weight = 27.92

Specific heat of Al = 0.20; combining weight = 9.033

Specific heat of Ag = 0.056; combining weight = 107.88

Calculate the true atomic weight of each of the three elements.

4. If the combining weight of C = 6, of N = 7, and of Cl = 35.45, from the table (p. 399) deduce the correct atomic weights.

5. Without looking up the weight of the gas, calculate the volume of  $\text{SO}_2$  that will be formed in the combustion of 15 g. of  $\text{FeS}_2$ .

6. What volume of  $\text{SO}_2$  will be generated by the action of HCl on 20 g. of sodium sulfite ( $\text{Na}_2\text{SO}_3$ )?

7. What volume of oxygen will be obtained by heating 50 g. of  $\text{KClO}_3$ ?

8. What volume of  $\text{H}_2\text{S}$  will be required to precipitate 20 g. of  $\text{CuS}$  from copper sulfate ( $\text{CuSO}_4$ )?

## CHAPTER XXV

### THE HYDROCARBONS ; COAL-TAR COMPOUNDS

**Introduction.** Carbon and hydrogen combine to form a large number of compounds known collectively as the *hydrocarbons*. For convenience these compounds are divided into a number of groups, or *series*, each one being named from its first member. In the table below are given the names and formulas of a few of the simpler members of the four most important series. It will be noted that the members in each series are arranged in accordance with the number of carbon atoms present. The general formula for the members of each series is added, in which the letter *n* represents the number of carbon atoms. The methane series is the most extensive, all the compounds up to  $C_{38}H_{78}$  being known.

#### METHANE SERIES

<i>Formula</i>	<i>Name</i>	<i>Boiling point</i>
$CH_4$ . . . . .	methane . . . . .	- 164.0°
$C_2H_6$ . . . . .	ethane . . . . .	- 84.0°
$C_3H_8$ . . . . .	propane . . . . .	- 44.1°
$C_4H_{10}$ . . . . .	butane . . . . .	- 0.3°
$C_5H_{12}$ . . . . .	pentane . . . . .	+ 37.0°
$C_6H_{14}$ . . . . .	hexane . . . . .	+ 69.0°
$C_7H_{16}$ . . . . .	heptane . . . . .	+ 98.4°
$C_8H_{18}$ . . . . .	octane . . . . .	+ 125.5°
$C_nH_{2n+2}$		

#### ETHYLENE SERIES

<i>Formula</i>	<i>Name</i>
$C_2H_4$ . . .	ethylene
$C_3H_6$ . . .	propylene
$C_4H_8$ . . .	butylene
$C_nH_{2n}$	

#### ACETYLENE SERIES

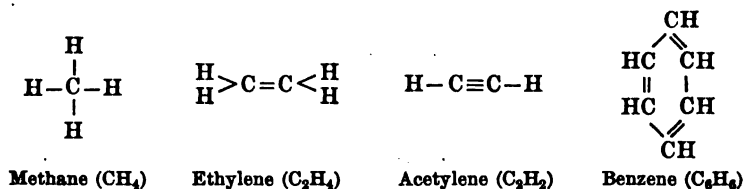
<i>Formula</i>	<i>Name</i>
$C_2H_2$ . . .	acetylene
$C_3H_4$ . . .	allylene
$C_nH_{2n-2}$	

#### BENZENE SERIES

<i>Formula</i>	<i>Name</i>
$C_6H_6$ . . .	benzene
$C_7H_8$ . . .	toluene
$C_8H_{10}$ . . .	xylene
$C_nH_{2n-6}$	

**Homologous series.** It will be noticed that the formulas of the successive members of each of the above series differ by the group of atoms  $\text{CH}_2$ . Such a series is called a *homologous series*. In general it may be stated that the members of a homologous series show a regular gradation in most physical properties and are similar in chemical properties. The boiling points, for example, gradually increase with the number of carbon atoms present. Thus, in the methane series the boiling points are such that under ordinary conditions of temperature and pressure the first four members are gases; those containing from five to sixteen carbon atoms are liquids, the boiling points of which increase with the number of carbon atoms present; those containing more than sixteen carbon atoms are solids.

**Structural formulas of the hydrocarbons.** The structural formula of the first member of each of the above series is as follows:



The hydrocarbons belonging to the methane series differ from those of the other series in that they do not unite directly with any other element or radical. In the case of methane this property is indicated by the structural formula assigned above, which represents the carbon atom as combined with four different hydrogen atoms. Since carbon is never known to have a valence greater than 4, it is evident, in accordance with the formula, that methane will not combine directly with any other element. Such compounds are known as *saturated* compounds. While other elements do not combine directly with saturated compounds, they may be *substituted* for elements already present. Thus, when chlorine acts upon methane under suitable conditions, one of the hydrogen atoms is displaced by a chlorine atom, forming a compound of the formula  $\text{CH}_3\text{Cl}$ .

Compounds like ethylene, on the other hand, are called *unsaturated*, for they combine directly with certain elements. Thus ethylene combines directly with chlorine, forming a compound

of the formula  $C_2H_4Cl_2$ . It might seem that this property of ethylene could best be expressed by the formula  $\begin{smallmatrix} H \\ H \end{smallmatrix} > C - C < \begin{smallmatrix} H \\ H \end{smallmatrix}$ , in which each carbon atom is tervalent. Since carbon tends to act as a quadrivalent element, one would expect a compound of this character to add directly the two atoms of chlorine, each carbon atom becoming thereby quadrivalent, as expressed in the formula  $\begin{smallmatrix} Cl \\ H \end{smallmatrix} > C - C < \begin{smallmatrix} Cl \\ H \end{smallmatrix}$ . It seems probable, however, that the carbon atoms in ethylene are really quadrivalent, and this fact is expressed by the *double union*, or, as it is often termed, the *double bond*, between the two carbon atoms. The addition of chlorine is then expressed as follows:  $\begin{smallmatrix} H \\ H \end{smallmatrix} > C = C < \begin{smallmatrix} H \\ H \end{smallmatrix} + Cl_2 \longrightarrow \begin{smallmatrix} Cl \\ H \end{smallmatrix} > C - C < \begin{smallmatrix} Cl \\ H \end{smallmatrix}$ . Similarly, in acetylene there is a *triple bond* between the two carbon atoms, and such a compound may add either two or four atoms of a univalent element.

**Petroleum.** Petroleum is the great source of the methane series of hydrocarbons. This liquid is pumped from wells driven into the earth in certain localities. Texas, California, Oklahoma, and Pennsylvania are the chief oil-producing regions in the United States. The crude petroleum consists largely of liquid hydrocarbons, in which are dissolved both gaseous and solid hydrocarbons. For most purposes it is refined before it is used. In this process the petroleum is run into large iron stills and subjected to fractional distillation. The various hydrocarbons distill over in the general order of their boiling points. The distillates which collect between certain limits of temperature are kept separate and serve for different uses; they are further purified, generally by washing first with sulfuric acid, then with an alkali, and finally with water.

Among the products obtained in the distillation of petroleum are the following, named in the order of their boiling points: *pentane*; *hexane*; the *naphthas*, of which there are several grades (see below); *kerosene*, or *coal oil*; *fuel oil*; *lubricating oils*; *vaseline*; and *paraffin*. Pentane is a definite compound and is

used as a standard illuminant in measuring the candle power of flames. Hexane, likewise a definite compound, is used as a solvent. The naphthas are mixtures of hydrocarbons distilling approximately between  $70^{\circ}$  and  $150^{\circ}$ , while kerosene distills between  $150^{\circ}$  and  $300^{\circ}$ . The oils that are semisolid at ordinary temperatures constitute vaseline. The liquid remaining after the higher-boiling oils have distilled is chilled, whereupon the solid constituents dissolved in the oil separate. These are filtered off and yield such products as paraffin and ceresin.

**The naphthas.** A number of different naphthas are recognized commercially, differing in boiling points and densities. Those of low boiling point are called *gasoline* and are used in gasoline engines and as a fuel; those of a higher boiling point are used in making paints. *Benzine* is a low-boiling naphtha, and, being a good solvent for such organic substances as fats and oils, is used in cleaning fabrics (dry-cleaning).

One should not confuse the two products, *benzene* and *benzine*: the former is a definite hydrocarbon,  $C_6H_6$ , obtained chiefly from coal tar, while the latter is a mixture of low-boiling hydrocarbons obtained from petroleum.

Because of the ease with which benzine burns, as well as of the explosive character of a mixture of its vapor with air, accidents often result from its use, especially when it is employed in our homes for cleaning fabrics. The greatest care must be taken in cleaning silk, since friction often causes a spark.

**The cracking of oils.** Formerly kerosene was the most important of the products obtained from petroleum. At present, however, gasoline is by far the most valuable, so that every effort is now made to increase the yield of gasoline. To accomplish this the distillation is carried on under conditions that tend to decompose the larger molecules making up the higher-boiling liquids into the simpler molecules which constitute liquids of lower boiling points. The process is known as the *cracking* of oils. It consists essentially in heating the oils or their vapors under pressure. It is of interest to note that it is possible in this way not only greatly to increase the yield of gasoline obtainable from a given sample of petroleum but also, by selecting proper conditions of temperature and pressure, to bring about reactions that result in the formation of certain hydrocarbons of the benzene series, especially benzene and toluene.

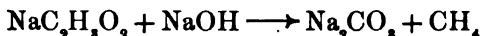
**Production of petroleum and its products.** The United States produces annually over 350,000,000 barrels of petroleum, which is about two thirds of the world's supply. This production does not meet our requirements, so that our reserve supply is being used and at such a rate as soon to exhaust it. On the average, the crude petroleum yields approximately the following

percentages of the chief products obtained from it: gasoline about 23 per cent, kerosene about 13 per cent, lubricating oils about 5 per cent, while gas and fuel oils constitute by far the largest amount, namely about 45 per cent. Some idea of the increase in gasoline consumption may be inferred from the fact that the gasoline production in the United States increased in the last ten years from 540,000,000 gallons to 3,500,000,000 gallons. It is evident from the above facts that the fuel problem is one of profound importance.

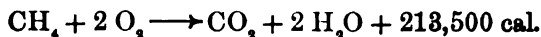
**Properties of the hydrocarbons.** The hydrocarbons are all readily inflammable, the carbon and hydrogen present combining with oxygen to form carbon dioxide and water respectively. The members of the methane series are very inactive compounds and, with the exception of oxygen, even the most active reagents have little effect upon them. The members of the other series are much more reactive. It is advisable here to discuss only a very few of the individual hydrocarbons.

**Methane (marsh gas) ( $\text{CH}_4$ ).** This hydrocarbon constitutes from 90 to 95 per cent of natural gas. It is formed in marshes by the decay of vegetable matter under water, and bubbles of the gas are often seen to rise when the dead leaves on the bottom of pools are stirred. It also collects in mines, and, when mixed with air, is called *fire damp* by the miners, because of its great inflammability, *damp* being an old name for a gas. It is formed when organic matter, such as coal or wood, is heated in closed vessels, and is therefore a principal constituent of coal gas.

Methane is prepared in the laboratory by heating sodium acetate with soda lime. The latter substance is a mixture of sodium and calcium hydroxides. Regarding it as sodium hydroxide alone, the equation for the reaction is as follows:

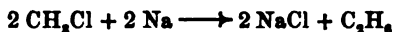


Methane is a colorless, odorless gas 0.55 times as heavy as air. It is but very slightly soluble in water. It can be condensed to a colorless liquid which boils at  $-164^\circ$  under a pressure of 1 atmosphere. It burns with a pale-blue flame, evolving heat, as shown in the following equation:



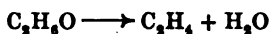
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**Ethane ( $C_2H_6$ ).** This hydrocarbon can be prepared from methane by first displacing an atom of hydrogen by one of chlorine, and then treating the resulting compound with sodium :



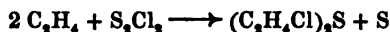
Ethane is similar to methane in properties.

**Ethylene ( $C_2H_4$ ).** Small amounts of ethylene are present in coal gas. It is prepared by the action of sulfuric or phosphoric acid on alcohol. In the reaction the alcohol loses the elements of water :

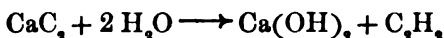


Commercially it is prepared by passing the vapor of alcohol through iron tubes filled with kaolin (aluminium silicate), heated to about  $500^\circ$ . The reaction is the same as that represented above, the kaolin acting as a catalytic agent.

During the war the United States prepared enormous quantities of ethylene for use in the manufacture of the poison liquid known as *mustard gas* ( $C_2H_4Cl$ )<sub>2</sub>S. This compound, while popularly called a gas, is really a high-boiling liquid. It is prepared by passing ethylene into sulfur monochloride, thus :

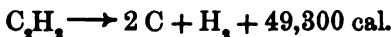


**Acetylene ( $C_2H_2$ ).** This is a colorless gas and is formed by the direct combination of carbon and hydrogen at very high temperatures. It is also formed when certain hydrocarbons are burned in a limited supply of air, so that the combustion is incomplete. In this way it is formed when the flame of a Bunsen burner "strikes back"; that is, when the flame burns at the bottom of the tube. The easiest as well as the most economical method for its preparation consists in the action of water upon calcium carbide :

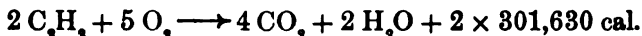


Acetylene, when pure, has a faint, rather pleasant odor. As ordinarily prepared, however, it has a disagreeable odor due to impurities. It is 0.92 times as heavy as air. At a temperature of  $0^\circ$  it is condensed to a colorless liquid by a pressure of 26.05 atmospheres. At lower temperatures it forms a solid melting at  $-81^\circ$ . It is an endothermic compound. In the formation of a gram-molecular weight of the gas 49,300 cal. are absorbed.

When the compound is decomposed, this same quantity of heat is evolved:



Acetylene, with the proper admixture of air, burns with a brilliant white light. The flame is very hot because to the heat of combustion of the carbon and hydrogen present there is added the heat of decomposition of the acetylene undergoing combustion:



When acetylene under some compression is subjected to the action of the electric spark, it is decomposed into carbon and hydrogen. In this way the Germans prepared much of the hydrogen used in filling the Zeppelins.

**The preparation and combustion of acetylene.** The gas can be prepared in a generator such as is shown in Fig. 126. The inner tube *A* contains lumps of calcium carbide, while the outer one is filled with water. As long

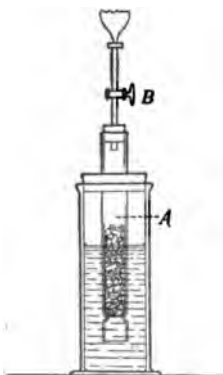


FIG. 126

as the stopcock *B* is closed, the water cannot rise in the inner tube. When the stopcock is open, the water rises and, coming into contact with the carbide, generates acetylene. The gas escapes through the stopcock. After the air has been expelled from the interior of the tube, the gas may be lighted as it issues from the burner.

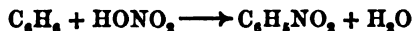
Acetylene is very explosive when subjected to pressure. It has been found that the gas can be compressed with safety, however, by forcing it at low temperatures into metal cylinders completely filled with some porous material such as a mixture of asbestos and cotton, which has been partially saturated with certain liquids (acetone, a liquid obtained by the destructive distillation of wood, is often used). These liquids absorb large volumes of the gas, and under such conditions it is not explosive. Stored in this way the gas is now a common article of commerce.

**Uses of acetylene.** As an illuminant, acetylene is often used in places where electric lights are not available. The chief use of the gas at present is in the cutting and welding of metals and in burning out the carbon deposited in the cylinders of gasoline engines. For these purposes acetylene is burned in pure oxygen

in a form of apparatus known as the *oxyacetylene blowpipe*, which is almost exactly like the oxyhydrogen blowpipe. A temperature of about  $2700^{\circ}$  may be obtained in this way. This blowpipe has been found especially useful in dismantling iron structures, since the flame heats the metal to a high temperature; then, by turning on an excess of oxygen, the metal is burned away. This makes it possible to cut large plates of metal into small pieces.

**The coal-tar compounds.** When coal is heated in the absence of air, as is done in the manufacture of coal gas and coke (see the following chapter), there is obtained, in addition to the gas and coke, ammonia (p. 252) and a thick tarry liquid known as *coal tar*. This liquid is composed of a mixture of a large number of compounds and serves as the commercial source of some 8 or 10 important ones. These are obtained from the coal tar by fractional distillation in a manner entirely analogous to that used in refining petroleum. Moreover, each of the compounds so obtained serves as the source material from which many other useful compounds are prepared. There are many thousands of these compounds, and all of them, whether obtained directly from coal tar or prepared from others so obtained, are known collectively as the *coal-tar compounds*. It is possible here to mention only a very few of the most important of these. These are as follows:

1. **Benzene ( $C_6H_6$ ).** This hydrocarbon is a colorless liquid boiling at  $80.2^{\circ}$ , and is a good solvent for most organic compounds, so that it is very useful in the laboratory. Both the liquid and its vapor are highly inflammable. One gram-molecule of the liquid on combustion evolves 749,200 cal., the water formed being in a state of vapor. Benzene differs from the other hydrocarbons studied in that it readily reacts with nitric acid. The product of the reaction is *nitrobenzene* ( $C_6H_5NO_2$ ), a slightly yellowish liquid often called oil of mirbane:



When nitrobenzene is reduced with hydrogen, a colorless liquid known as *aniline* is formed. This has the formula  $C_6H_5NH_2$  and is the compound from which many of the *aniline dyes* are prepared.

2. **Toluene ( $C_7H_8$ ).** This is a liquid boiling at  $110^{\circ}$  and resembles benzene in its general properties. When oxidized, it forms *benzoic acid*, the sodium salt of which (sodium benzoate) is a common food preservative.

When treated with nitric acid it forms tri-nitrotoluene,  $C_7H_5(NO_2)_3$ . This is a white crystalline solid commonly known as T. N. T. It constituted the principal explosive used in the World War. From toluene there is also prepared the white solid known as *saccharine*, which is over 500 times as sweet as sugar. This was formerly used in foods as a sweetening agent, but in 1912 the government forbade its further use for that purpose.

3. *Naphthalene* ( $C_{10}H_8$ ). Ordinary moth balls are nearly pure naphthalene. The hydrocarbon is also used in making the well-known dye *indigo*. Formerly this dye was obtained from the indigo plant which was cultivated in India, and a limited amount is still obtained from this source. Most of our supply, however, is prepared either from naphthalene or benzene.

4. *Anthracene* ( $C_{14}H_{10}$ ). This hydrocarbon is a nearly white solid and is used in the manufacture of *alizarin*, — an important dye formerly obtained from the root of the madder plant, which was grown in France on a large scale for this purpose.

5. *Phenol* (*carbolic acid*) ( $C_6H_5OH$ ). This is a white crystalline solid, very caustic and poisonous. It is the source material for the preparation of *salicylic acid*. It is also used in the manufacture of *bakelite* and *condensite*. These are commercial products used in making such articles as buttons, umbrella handles, pipestems, and insulators in electrical apparatus. When treated with nitric acid phenol forms picric acid ( $C_6H_2(NO_2)_3OH$ ), a yellow solid which was used extensively as an explosive in the World War.

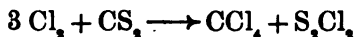
6. *Cresol* (*cresylic acid*) ( $C_7H_7OH$ ). There are three isomeric cresols. A mixture of these is obtained directly from coal tar and constitutes the basis of most of the disinfectants now on the market.

**Substitution products of the hydrocarbons.** As a rule, at least a part of the hydrogen in any hydrocarbon can be displaced by certain elements or groups of elements. Thus the compounds  $CH_3Cl$ ,  $CH_2Cl_2$ ,  $CHCl_3$ , and  $CCl_4$  can be obtained from methane by the action of chlorine. Such compounds are called *substitution products*. Among the important substitution products of methane are the following:

1. *Chloroform* ( $CHCl_3$ ). This is a well-known compound used as an anesthetic in surgery. It is a colorless, heavy liquid boiling at  $61^\circ$ . If the hydrogen present is displaced by the radical  $NO_2$ , there is formed *chloropicrin* ( $CNO_2Cl_2$ ), a liquid used very largely in the World War as a toxic gas.

2. *Iodoform* ( $CHI_3$ ). Iodoform is a yellow crystalline solid, largely used as an antiseptic in surgery.

8. *Carbon tetrachloride* ( $\text{CCl}_4$ ). This compound is a heavy colorless liquid boiling at  $76.7^\circ$ . It is prepared by the action of chlorine on carbon disulfide:



Like chloroform and benzene, it is a good solvent for many organic compounds, such as the fats, and is used for this purpose, as, for example, in removing grease spots from fabrics. Its main use is as a fire extinguisher, being sold for this purpose under the name of *pyrene*.

### QUESTIONS

1. Write the formulas for the compounds formed by the addition of chlorine to acetylene.
2. How could you distinguish between gasoline and kerosene?
3. How do the various hydrocarbons differ in properties? In what respect are they all alike?
4. Marsh gas is formed by the decay of vegetable matter under water. What is the function of the water?
5. Do you see any reason why benzene could not be used in place of gasoline in a gasoline engine?

### PROBLEMS

1. Contrast the number of calories of heat generated by the combustion of 100 l. each of hydrogen, methane, and acetylene; also by 100 g. of each.
2. What weight of methane would be required to furnish sufficient heat to change 1 kg. of water at  $20^\circ$  into steam at  $100^\circ$ ?
3. (a) What volume of oxygen is required for the combustion of 100 l. of methane? (b) How would the volume of the carbon dioxide formed compare with the volume of the methane burned?
4. Suppose that a given sample of gasoline is composed of equal weights of heptane ( $\text{C}_7\text{H}_{16}$ ) and octane ( $\text{C}_8\text{H}_{18}$ ). What volume of oxygen is necessary for the combustion of 10 kg. of this gasoline?
5. What weight of benzene would be required for the preparation of 100 kg. of aniline?
6. Phenol sells for about 12 cents a pound. What is the cost of sufficient phenol to make 100 tons of picric acid?

## CHAPTER XXVI

### FLAMES; FUEL GASES; EXPLOSIONS

**Visible combustion.** When combustion proceeds rapidly, the heat liberated is readily perceived, and, as previously stated, the reaction is accompanied by light. The products of combustion may be solids, as in the case of metals such as iron; or they may be liquids, as in the case of hydrogen; or gases, as with carbon and sulfur. If the burning substance is a solid at the temperature of combustion, it may become incandescent, but there is no flame. This is the case with the combustion

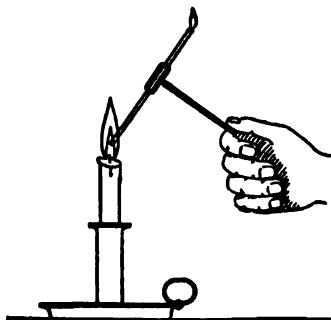


FIG. 127

of pure carbon and many of the metals. When both of the substances concerned in the combustion are gases, the bounding surface between the two presents the appearance known as a flame, and this flame is usually, though not always, distinctly luminous. The fact that a flame often accompanies the combustion of solids (such as coal, wood, or a candle) or of liquids (such as oils) does not contradict

the statements just made. It can be shown that in each case the heat of combustion produces vapors from the burning solid or liquid, and these in turn burn with a flame. If one end of a slender glass tube is held in the base of a candle flame, as indicated in Fig. 127, a flame is formed when a light is applied at the other end, showing that gases which can be drawn off and ignited separately are produced from the candle. The blue flame over a bed of coals is the flame of burning carbon monoxide formed by the combustion of the carbon.

**Fuel gases.** Before considering the structure of flames it will be of advantage to have before us the general chemical characteristics of the gases whose combustion gives rise to the most familiar examples of flames. A number of varieties of gases are now employed as sources of heat, light, and power.

1. *Coal gas.* It has been known for several centuries that when soft, or bituminous, coal is heated out of contact with air, combustible gases are formed; indeed, gas obtained in this way was used for street lighting in London and Paris more than a hundred years ago.

**The manufacture of coal gas.** The manufacture of coal gas is represented in a diagrammatic way in Fig. 128. The coal is introduced into a closed retort *A* and heated by the fire below. A number of these retorts are placed in horizontal rows, each being furnished with a delivery pipe. This delivery

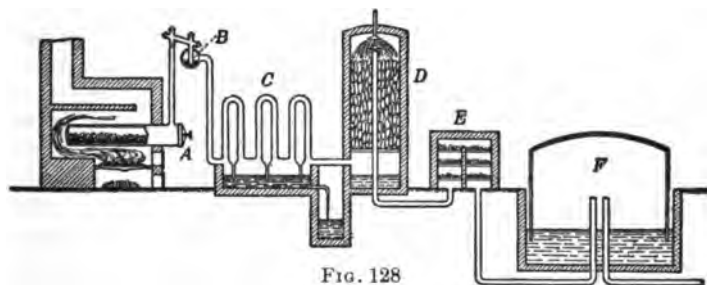


FIG. 128

pipe leads into a large pipe *B* (known as the *hydraulic main*), which runs at right angles to the retorts. The application of heat causes the coal to undergo complex changes which result in the formation of a large number of compounds. These compounds escape through the delivery pipe into the hydraulic main. The temperature being reduced, a small amount of the products that are solid or liquid at ordinary temperatures condense in the hydraulic main in the form of a thick tarlike mass known as *coal tar*. The gases then pass on into the cooler *C*, in which the products are cooled to such an extent that the remaining tar is largely deposited. Along with the tar there is condensed a liquid (chiefly water) containing ammonia in solution and known as *ammoniacal liquor*. The gas is then led into the scrubber *D*, where it passes through a column of loose coke, over which water is sprayed. Here the gas is still further cooled and to some extent purified from soluble gases, such as hydrogen sulfide and ammonia. In the purifier *E* it passes over a bed of lime or of iron oxide, which removes

the remainder of the sulfur compounds, and from this it enters the large gas holder *F*, from which it is distributed to consumers.

The great bulk of the carbon remains in the retort as *coke* and as *retort carbon*. The yield of gas, tar, and soluble materials depends upon many factors, such as the composition of the coal, the temperature employed, and the rate of heating. One ton of good gas coal yields approximately 10,000 cu. ft. of gas, 1400 lb. of coke, 120 lb. of tar, and 20 gal. of ammoniacal liquor. Not only is the ammonia obtained in the manufacture of the gas of great importance, but the coal tar is the source of many useful substances, as already explained in the preceding chapter.

**The by-product coke oven.** It will be observed that coke is formed in the process used in the manufacture of coal gas. Coke is a very important product and is used in large quantities, especially in the reduction of metals, such as iron, from their ores. The quantity of coke obtained in the manufacture of coal gas has never been sufficient to meet the demand. The additional coke required has been prepared for the most part by coking the coal in ovens, called *beehive ovens* because of their shape. The coking of coal in these ovens is carried out as follows: The oven is nearly filled with coal and the coal is ignited. After the fire is well started the draft is shut off, and the heat formed in the combustion of a portion of the coal is sufficient to coke the remainder of the coal. In this process all the coal tar, coal gas, and ammonia escape through an opening in the top of the furnace and are lost. The growing demand for ammonia, as well as for the products obtained from coal tar, has led to the construction of furnaces or ovens for the coking of coal, which make it possible to save the coal tar and ammonia formed in the process. Such ovens are known as *by-product coke ovens*, this term being chosen because the ammonia and coal tar formed in the process of coking the coal are by-products, the coke being the main product. These ovens are very much more complex than the beehive ovens, but the demand for ammonia and coal tar is rapidly becoming so great as to cause the gradual introduction of the by-product ovens, which now surpass the beehive ovens in production of coke.

In the manufacture of coal gas stress is laid upon the yield of gas; while in the by-product oven the emphasis is placed upon the yield of coke. The difference in the results obtained is due mainly to the difference in the grade of coal selected, as well as in the heat treatment. Fig. 129 represents a cross section of a part of a row of by-product ovens. The ovens *A* are placed side by side, and separated from each other by the combustion chambers *B*. The ovens are made of silicious material and are narrow, so that the heat can penetrate the coal with which they are filled. The fuel used, as a rule, is the gas generated in the process. A high temperature is secured by preheating the air used in combustion. This is done by having two sets of compartments *C*, loosely filled with

bricks. First, the hot products of combustion are led from the heating chambers *B*, through one set of the compartments *C*, until the bricks become very hot. The hot gases are then diverted through the second set of compartments, while the air required for combustion is led over the hot bricks into the heating chamber, where it meets the necessary supply of

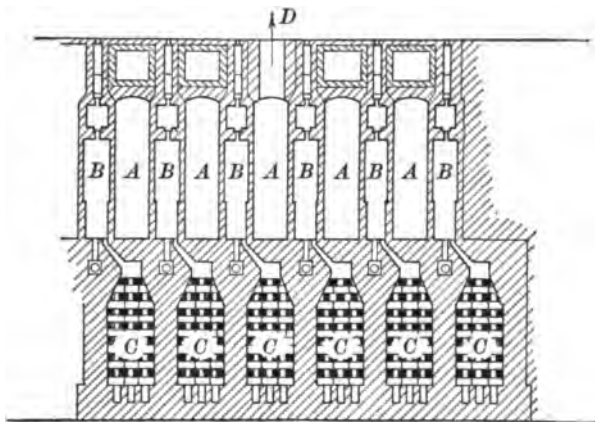
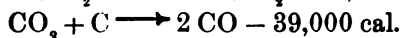
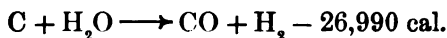


FIG. 120

coal gas. By the time the bricks in the first set of compartments are cool, those in the second set have become heated and the flow of gases is interchanged. The gaseous products formed in the coking of the coal escape through the pipe *D*, and are separated and purified much as in the process for making coal gas.

2. *Water gas.* Water gas is essentially a mixture of carbon monoxide and hydrogen. It is manufactured by passing superheated steam over very hot anthracite coal or coke, the chief reactions being expressed in the following equations:



The industrial process is intermittent. The fuel is burned with a forced draft in a suitable furnace until it is very hot. The air is then shut off and the steam turned on until the temperature falls to about 1000°. The process is then reversed. The fall in temperature is rapid, partly owing to radiation and to the cooling occasioned by the steam, but largely because of the endothermic character of the reactions. The gas so formed contains the nitrogen which was in the furnace when the steam was admitted.

Water gas burns with a pale-blue, nonluminous flame. It is very poisonous and has no odor. To make it suitable for illumination in an ordinary burner, as well as to give it an odor and so make it safer, it must be enriched with hydrocarbons called *illuminants*. This is accomplished by passing the gas through a furnace filled with hot fire brick upon which crude petroleum is sprayed. The petroleum oils are decomposed (cracked) into simpler gaseous bodies, the most important of which are methane, acetylene, and ethylene. Coal gas is sometimes enriched in a similar way by adding petroleum to the coal in the retorts.

**Commercial manufacture of hydrogen.** Under the discussion of the methods used for the synthetic preparation of ammonia (p. 250) the statement was made that hydrogen is caused to combine directly with nitrogen. The hydrogen required in the process is prepared by the action of steam on carbon under appropriate conditions. It will be seen from the reactions taking place in the manufacture of water gas that the first products of the reaction are carbon monoxide and hydrogen. If this mixture of gases is

passed, together with steam, over a catalyzer (iron oxide is generally used) the carbon monoxide and steam react thus:



In this way a mixture of hydrogen, carbon dioxide, and a small percentage of carbon monoxide is obtained. The two oxides of carbon are then removed by appropriate absorbents, leaving the pure hydrogen.

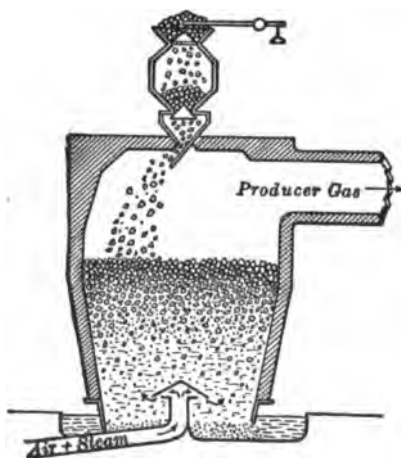


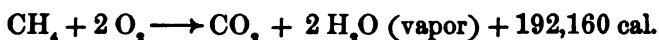
FIG. 180

**3. Producer gas.** Producer gas is used in connection with many metallurgical furnace operations and also as a fuel for gas engines. It is

made by burning coal under such conditions that the product of combustion is largely carbon monoxide (Fig. 180). Very often a little steam is admitted with the air, and this on passing through

the hot bed of coals is reduced as in the preparation of water gas. Made in this way, producer gas is composed mainly of carbon monoxide, hydrogen, and nitrogen. It can be made from coal of a poor quality, even from lignite, and as gas engines run well with this gas, it furnishes the most economical method for utilizing low-grade coal for power.

4. *Natural gas.* In many regions of the United States, as well as in other countries, natural gas is obtained from wells drilled into a stratum holding the gas. While it is variable in composition, it consists largely of methane, many samples containing as much as 95 per cent of this compound. It burns with a flame of moderate luminosity, but works well with a gas mantle. It has a high heat of combustion, as shown in the following equation:



It is an ideal fuel and is often conducted through pipes for hundreds of miles from the gas fields to cities.

The natural gas from some wells contains a considerable amount of hexane and heptane. When this gas is compressed and cooled, these separate in liquid form and constitute a high-grade gasoline known commercially as *casinghead gasoline*.

**Comparative composition of gases.** The following figures are the results of analyses of average samples, but since each kind of gas varies considerably in composition, the values are to be taken as approximate only. The nitrogen and traces of oxygen are derived from the air.

COMPOSITION OF GASES BY VOLUME

	OHIO NATURAL GAS	COAL GAS	WATER GAS	ENRICHED WATER GAS	PRODUCER GAS
H <sub>2</sub> . . . . .	0.0	41.3	52.88	37.96	10.90
CH <sub>4</sub> . . . . .	89.5	43.6	2.16	7.09	
C <sub>2</sub> H <sub>6</sub> . . . . .	9.3			2.01	
C <sub>2</sub> H <sub>2</sub> + C <sub>2</sub> H <sub>4</sub> . . . . .	0.3	3.9		9.40	0.60
CO . . . . .	0.4	6.4	36.80	32.25	20.10
CO <sub>2</sub> . . . . .	0.3	2.0	3.47	4.73	8.50
N <sub>2</sub> . . . . .	0.2	1.2	4.69	3.96	59.90
O <sub>2</sub> . . . . .	0.0	0.3		0.60	
Other hydrocarbons . .	0.0	1.5		1.80	

**Relation of the two gases to the flame.** The gas issuing from the burner is said to *undergo* combustion, while that one which constitutes the atmosphere about the flame is said to *support* combustion. These terms are entirely conventional, since the relation of the two gases may be reversed without greatly altering the appearance of the flame.

**Apparatus.** Fig. 131 illustrates a convenient apparatus for demonstrating this fact. A wide lamp chimney *A* is covered with a piece of asbestos board *B*, which has a hole in the center about as large as a dime. A

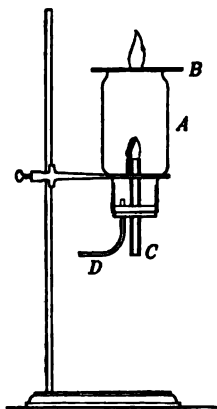


FIG. 131

straight tube *C*, about 1 cm. in diameter, and also a smaller tube *D* connected with the gas supply, passes through a cork at the bottom. If the hole in *B* is closed (by a piece of asbestos board) while gas is admitted through *D*, the excess gas escapes downward through *C*, where it may be lighted. The hole in *B* is now opened, and at once the flame ascends to the top of the tube *C*. This flame is produced by air, drawn up through *C*, burning in an atmosphere of coal gas. Finally, the excess of coal gas may be ignited at *B*, where it will burn in air, the two flames being very similar.

**Gas mantles.** In using the fuel gases as illuminants the gas is usually mixed with air before burning. In this way the gas burns with a hot but nearly nonluminous flame. The light is obtained by suspending about this flame a gauze mantle of suitable material. The best mantles are composed of a mixture of 99 per cent of thorium oxide with 1 per cent of cerium oxide.

The thorium and cerium compounds used in gas mantles are obtained from *monazite sand* found principally in Brazil. The process of making a gas mantle consists in knitting a tubular fabric, which is then dipped into a solution of the nitrates of thorium and cerium. After being dried the fabric is heated, in which process the yarn is burned, while the nitrates of thorium and cerium are converted into oxides which are left in the form of the original fabric. The resulting mantle is very delicate and is strengthened for shipping by dipping it into a solution of an appropriate substance and drying.

**Products of the combustion of ordinary fuels.** Ordinary fuels, such as oil, wood, coal, and fuel gases, are largely made up of carbon and hydrogen or their compounds. The chief products

of the combustion of such fuels are carbon dioxide and water. Associated with these are small amounts of other products, such as carbon monoxide and sulfur dioxide, the latter being formed from traces of sulfur compounds in the fuels.

Rooms are not infrequently heated by gas or oil stoves, with no provisions for removing the products of combustion. Likewise, natural gas is often burned in stoves or grates with the damper closed so as to leave no opening into the chimney. Such practices are greatly to be condemned, since the air in the rooms heated in this way soon becomes so contaminated with the various products of combustion as to render it unfit for respiration. The large amount of water vapor formed in rooms so heated condenses on the windows in cold weather, causing the glass to *sweat*.

**Structure of a flame.** The structure of a flame can be studied to the best advantage when the combustible gas issues from a round tube into an atmosphere of the gas supporting combustion (usually the air), as is the case with an ordinary Bunsen burner (Fig. 132). Under these conditions the flame is conical in outline.



FIG. 132

**Simple flames.** When the chemical action taking place in the combustion is the mere union of two gases, as is true in the union of hydrogen or carbon monoxide with oxygen, or hydrogen with chlorine, the structure of the flame is very simple. It consists of two superimposed cones of different altitudes. The inner one may be shown to be merely unchanged cold gas, and is therefore not a real part of the flame. A match head suspended in this region (Fig. 132) before lighting the gas is not ignited by the flame around it.

**Complex flames.** In the burning of hydrocarbons, as well as of many other gases, the flame is more complex, and as many as four distinct cones may be seen (Fig. 133). The innermost one, *A*, is really not a part of the flame, being formed of gas not

yet brought to the point of combustion. If a Bunsen burner is employed, with the ring at the base turned to admit plenty of air, the second cone *B* is sharply defined and is bluish green in color. If the burner tube is wide, or too much air is admitted, the rate of combustion in this cone may exceed the rate of flow of the gas, in which case the cone will travel down the tube and burn at the base, or *strike back*. As the air is shut off it will be seen that a luminous spot appears at the apex of this cone, which gradually takes the form of a cone *C*, quite covering the inner one and brightly luminous over all its surface. Finally, if some object is held so as to intercept the light from this region, it will be seen that there is a fourth cone *D*, which is only faintly luminous.

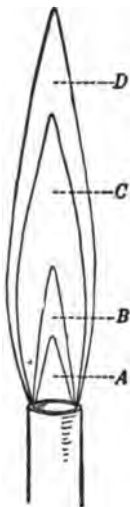


FIG. 133

**Cause of the cones.** Since the gases which give rise to multiplication of cones on combustion are always chemical compounds, such as hydrocarbons, it would appear probable that the cones are due to successive chemical reactions taking place in different regions. Smithells devised a very simple method for separating the two principal cones and ascertaining the character of the combustion in each one. The essentials of his apparatus are shown in Fig. 134.

**Analysis of flames.** The tube *A* of an ordinary Bunsen burner is extended in length by a glass tube *B* of slightly greater diameter. A wider tube *C*, of about 2 cm. diameter and provided with a side tube *D*, surrounds this tube, to which it is connected by a cork *E*, which slips readily on the smaller tube. The wide tube *C* is slipped down until the ends of the two tubes are even; the gas is turned on and lighted at the top of these tubes, where it burns with a double cone. Air is admitted at the base of the burner until the inner cone is sharply defined and is bluish green in color.

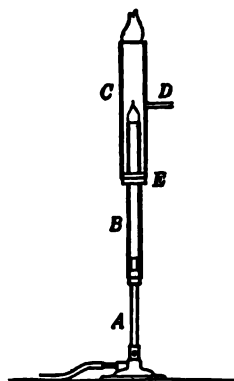


FIG. 134

The outer tube is then pushed up, carrying the outer cone with it and leaving the inner one upon the rim of the smaller tube, as shown in the figure. The two cones are widely separated in this way, and the space between them becomes filled with the gases formed by the combustion in the inner cone. These can be drawn off through the side tube *D* and analyzed.

**Reactions in flames.** In this way Smithells showed that in the inner cone the original hydrocarbons burn to form carbon monoxide and hydrogen, together with some unsaturated hydrocarbons, chiefly acetylene and ethylene. In the second, or luminous, cone the hydrogen and carbon monoxide are in part burned by the oxygen supply in the atmosphere, while the illuminants, acetylene and ethylene, are decomposed into carbon and hydrogen, the separated carbon becoming brilliantly incandescent. It quickly undergoes combustion, however, and the outer edge of the luminous flame marks its disappearance. The outside, faint mantle is the region in which the combustion of carbon monoxide and hydrogen is completed.

**Causes affecting luminosity.** While the process just sketched accounts for the luminosity of flames in a general way, there are evidently a number of other factors which must be taken into account. Some flames, such as that of burning ammonia, are luminous, though there is no solid incandescent product formed during combustion. It is possible that, in the decomposition into elements at a high temperature, endothermic bodies may give up some of their energy directly as light rather than as heat.

The temperature of the gases before combustion also affects luminosity. The nonluminous flame of a Bunsen burner becomes somewhat luminous when the tube of the burner is strongly heated. When the gas or the flame itself is cooled, the luminosity diminishes, as may be seen by bringing a large mass of cold metal, such as a flatiron, close to a luminous flame. A loose spiral of heavy copper wire brought down over a luminous Bunsen flame acts in the same way (Fig. 185).

The concentration of the gases is also an important factor, the luminosity being greater as the concentration increases.

Consequently, pressure increases luminosity, as is shown by the fact that hydrogen under pressure burns in oxygen (also under pressure) with a luminous flame. On the other hand, dilution with an indifferent gas, especially if it is cold, greatly reduces luminosity. Carbon dioxide, nitrogen, or even air, admitted at

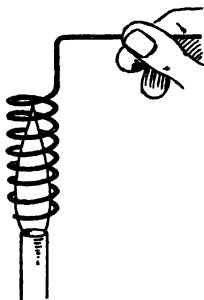


FIG. 135

the base of a luminous flame, destroys the luminosity. Such gases evidently act by diminishing the rapidity of combustion, and consequently the heat per unit of time, and by absorbing heat and so reducing the temperature still farther.

**The temperature of flames.** The actual temperature which can be realized in an ordinary flame obviously depends upon many conditions, such as the composition of the gas, its pressure, temperature, and rate of flow, and the method of supplying the air. Even in an ordinary Bunsen flame burning under favorable conditions it is very difficult to determine the maximum temperature attained. The actual region of great heat is very limited, as the burning zones are very thin. The temperature in different parts of the flame is very different, and any object placed in the flame, for determining its temperature, cuts across many different regions and is unequally heated. Evidently the temperature is much higher than that recorded by a body in the flame, since the specific heat of solids is so much greater than that of gases. Under exceptional conditions it has been found possible to melt a very fine platinum wire in a good Bunsen flame so that a temperature of  $1755^{\circ}$  is surely reached. The accompanying diagram (Fig. 136) gives a rough estimate of the probable temperature in various parts of a good nonluminous Bunsen flame.

**Reducing and oxidizing flames.** Since the region just below the luminous cone is very hot and contains the reducing gases hydrogen and carbon monoxide, a substance such as a metallic oxide, placed in this region, will undergo reduction, provided

it can be reduced by such hot gases. This region is therefore called the *reducing region*, and a body heated in this way is said to be heated in the *reducing flame*. At the apex of the flame there are no reducing gases, but it is very hot and air is abundant; consequently a substance which is rather readily oxidized will undergo oxidation if heated in this region. This is called the *oxidizing flame*.

**Explosions.** An explosion is caused by the sudden change in the volume of gases following chemical reaction or as the result of the formation of gases from liquid or solid materials. The greater the volume change, and the more rapidly it is produced, the more violent the explosion.

The equation of the reaction does not always supply the information necessary for predicting an explosion. Thus, when 2 volumes of hydrogen and 1 of oxygen are mixed and ignited, 2 volumes of water vapor are formed, which is not a great volume change. Taking into account the heat evolved, however, the complete equation is as follows:



If we remember Gay-Lussac's law of gas expansion, and recall the fact that the specific heats of gases are very small, we shall see that the heat of reaction may lead to an expansion of 5 or 6 volumes, especially when the reaction is very rapid.

**Explosive mixtures.** A second fact not indicated by the equation of a reaction is that explosion of a gas mixture will not occur unless the mixture falls between certain limits in percentage composition. Thus, if hydrogen and air are mixed, the resulting mixture is not explosive unless the volume percentage of hydrogen is above 10 per cent and below 66 per cent. In

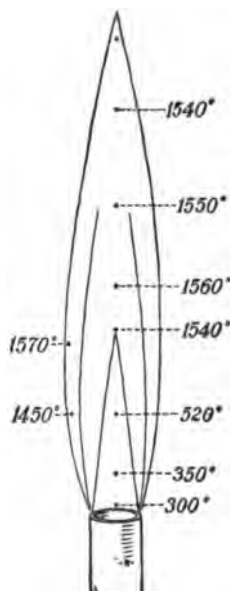


FIG. 136

mixtures outside of these limits the combination is so slow, the heat is so largely absorbed by the excess gases present, and the volume change takes place so slowly and is so small a fraction of the total volume that no explosion occurs. The following table gives both the lower and the upper limits of explosive mixtures of several gases with air, expressed in volume percentages. The values are to be regarded as roughly approximate.

## EXPLOSIVE MIXTURES

GAS	VOLUME PERCENTAGE AT LOWER LIMIT	VOLUME PERCENTAGE AT HIGHER LIMIT
Hydrogen . . . . .	10.00	66.00
Methane . . . . .	5.5	14.5
Carbon monoxide . . . . .	15.00	73.00
Acetylene . . . . .	2.53	73.00
Water gas . . . . .	9.00	55.00
Coal gas . . . . .	6.00	29.00

**Mine explosions.** In many coal mines methane collects at times and is called *fire damp*. It forms an explosive mixture with air when the percentage of methane rises above 5.5 per cent. In the reaction the oxygen of the air is decreased and the carbon dioxide is increased to such a point that the air will no longer support respiration. The gases resulting from the explosion are called *choke damp*, and often suffocate the miners.

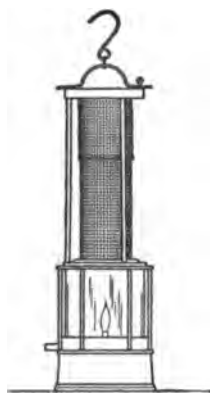


FIG. 137

**Safety lamp.** Fortunately the ignition point of fire damp is high and its flame may be extinguished by cooling. In 1815 Sir Humphry Davy invented a miner's lamp, based on this principle, in which the usual chimney of a lantern is replaced by a wire gauze (Fig. 137).

An explosion flame starting at the wick is so cooled by the metal wire that ignition ceases and the explosion is confined to the interior of the lamp. The principle may be demonstrated

by holding a wire gauze a few inches above a Bunsen flame parallel with the table (Fig. 188). When the gas is turned on and a light is applied above the gauze, the resulting flame rests upon the gauze, but does not pass through it to the burner.

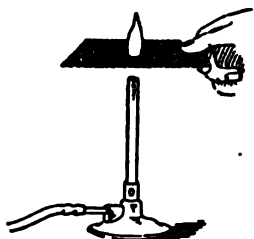


FIG. 188

**Dust explosions.** In dry mines great quantities of fine coal dust collect if the mine is not kept damp by spraying. A blast may blow this into the air, and the result may be an explosion due to the union of carbon and oxygen:



Moreover, the carbon monoxide, called *afterdamp*, is also explosive when mixed with air, and is very poisonous. Following an explosion in a mine, rescuers often carry live birds with them, as these are extremely sensitive to the poisonous effects of carbon monoxide, and their death warns the rescuers of their own peril.

In a similar way severe explosions have resulted in flour mills and woodworking plants from the fine combustible dust floating in the air, so that in modern mills all machinery producing such dust is covered by a hood in which a strong draft is maintained.

**The electric furnace.** In recent years electric furnaces have come into wide use in operations requiring a very high temperature. Temperatures as high as 3500° can be easily reached, whereas the hottest oxyhydrogen flame is not much above 2000°. These furnaces are constructed on one of two general principles.

1. **Arc furnaces.** In the one type the source of heat is an electric arc formed between carbon electrodes separated a little from each other, as shown in Fig. 139. The substance to be heated is placed in a vessel, usually a graphite crucible, just below the arc. The electrodes and crucible are surrounded by materials which fuse with great difficulty, such as magnesium oxide, the walls of the furnace being so shaped as to reflect the heat downwards upon the contents of the crucible.



FIG. 139

2. *Resistance furnaces.* In the other type of furnace the heat is generated by the resistance offered to the current in its passage through the furnace. In its simplest form it may be represented by Fig. 140. The furnace is

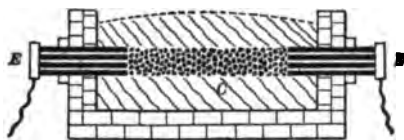


FIG. 140

merely a rectangular box built up of loose bricks. The electrodes *E, E*, each consisting of a bundle of carbon rods, are introduced through the sides of the furnace. The materials to be heated (*C*) are filled into the furnace up to the electrodes, and a layer of broken

coke is arranged so as to extend from one electrode to the other. More of the charge is then placed on top of the coke. In passing through the broken coke the electrical current encounters great resistance. This generates much heat, and the charge surrounding the coke is brought to a very high temperature. The advantage of this type of furnace is that the temperature can be regulated to any desired intensity.

### QUESTIONS

1. In the commercial manufacture of hydrogen what absorbents would you suggest for the removal of the oxides of carbon?
2. Suggest methods for preventing the "sweating" of windows.
3. Give the advantages and disadvantages of water gas as an illuminant.
4. (a) Contrast the different fuel gases as to amounts of hydrogen and methane present. (b) Which of the fuel gases would you expect to have the least heat value?
5. What properties should the metal gauze used in the safety lamp possess?
6. Give the relative advantages for the manufacture of coke by each of the three methods discussed.

### PROBLEMS

1. Calculate the relative volumes of the carbon monoxide and hydrogen formed according to the equation  $C + H_2O \longrightarrow CO + H_2$ . Compare your results with the composition of water gas as given in the table on page 421. Account for the difference.
2. Suppose that water gas consists of equal volumes of carbon monoxide and hydrogen. What amount of heat will be generated by the combustion of 1000 l. of this gas at  $20^\circ$  and 760 mm.?

3. Suppose that water gas consists of equal volumes of carbon monoxide and hydrogen and that natural gas is composed of pure methane. Contrast the heating value of equal volumes of the two gases.

4. A room  $5 \times 6 \times 3$  meters is heated by a portable gas stove burning 10 cu. ft. of gas per hour. (a) If the gas consumed is pure methane, what weight of combustion products are formed in five hours? (b) What will be the volume of the carbon dioxide formed at  $20^\circ$  and 740 mm.? (c) How will this compare with the volume present in normal air in a room of the above dimensions?

5. (a) How many liters of oxygen will 100 l. of methane require for its combustion? (b) Contrast the volumes of the methane and oxygen with the volumes of the products formed, all being measured under the same conditions of temperature and pressure. (c) Why should an explosion of natural gas shatter a building?

## CHAPTER XXVII

### THERMOCHEMISTRY

**Introduction.** In many places throughout the preceding pages emphasis has been placed upon the heat changes that accompany the various transformations of matter, whether they are distinctively chemical in character or are like those changes in state that we are apt to regard as more nearly physical. The experimental measurement of these heat changes, together with the formulation of laws regarding them, constitute a branch of chemistry called *thermochemistry*.

**Source of the heat of a reaction.** When two atoms of any kind enter into combination, or are parted from existing combination, we can hardly doubt that the process involves an alteration in the structure of all the atoms taking part in the reaction. These changes will either liberate energy or absorb it, according to whether the product represents a more stable or a less stable grouping in atomic structure. We must also think that each atom is surrounded by a field of electrical forces, and that it occasions changes in energy to bring two atoms into reaction against such forces.

Similarly, when two molecules of any kind act upon each other in any way, more or less profound changes in structure must take place, with evolution or absorption of energy. In either case this liberated or absorbed energy is usually manifest as heat, though by the proper devices it may appear in other forms, notably as electrical energy.

**Quantity of heat different for each reaction.** Since no two reactions result in identical changes in structure, no two produce the same change in energy. Consequently, the heat change is different for each separate reaction.

It might be thought that each kind of an atom has a definite quantity of heat energy that it can give off as a result of chemical action, and that we should be able to measure this and assign it to the atom as a constant, just as we measure the mass of the atom and arrive at the atomic weight as a constant. A little reflection will show the fallacy of such an idea. In all cases the heat energy comes from at least two atoms and is a mutual contribution. Each chemical reaction results in different changes within the atoms, and each atom may undergo a variety of changes in internal structure.

We cannot tell what energy carbon possesses, but can only say how much is liberated when it combines with hydrogen or oxygen or some other element. So all we can do at present is to measure the heat change in each reaction and regard it as a purely experimental constant belonging to the reaction.

**Heat of reaction not proportional to affinity.** While the heat of a reaction often gives us a clear idea as to the intensity of the chemical affinity between two substances, this is not always so. This fact may perhaps be made clearer by a gravitational analogy. In general the intensity of the earth's attraction for a falling body may be measured by the shock produced when the body strikes the earth, for the pull of gravity will be proportional to the mass of the body. But if the falling body happened to be a stick of dynamite, we should draw a false inference as to its mass if we measured it by the shock produced.

**Endothermic compounds.** That affinity is not proportional to heat evolution is clearly demonstrated by the existence of many endothermic compounds. Thus we have the reaction



If the heat of formation were to be taken as a direct measure of chemical affinity, there should be less than no affinity between the elements of such a compound, and therefore no force to hold them together; yet many endothermic bodies, such as carbon disulfide and acetylene, are fairly stable under ordinary conditions.

**The measurement of heat of reaction.** Two general types of calorimeters are employed in measurements of the heat of reactions. In reactions taking place in solution the open calorimeter described on page 8 may be used. In a reaction involving combustion, where a gaseous substance must be supplied to maintain the action, a bomb calorimeter is used.

**Bomb calorimeter.** This is a strong steel flask lined with platinum or some other noncombustible material and provided with a tight-fitting screw cap (Fig. 141). In determining the heat of combustion a weighed sample of the substance is placed on the capsule *A*, oxygen is admitted through

the tube *B* until the pressure in the bomb is about 20 atmospheres, and the bomb is then closed and placed in an open calorimeter. The charge is ignited by passing an electric current through the fine iron fuse-wire (*C*) stretched above the charge. The wire is melted and the red-hot drop of burning metal falls upon the charge, igniting it. The heat given off during combustion is measured by the rise in temperature of the water surrounding the bomb, which is stirred by the stirrer *D*. A preliminary experiment must be made upon a weighed charge of a substance whose heat of combination is known (such as cane sugar), to determine the heat absorbed by the bomb, together with that due to the melting and combustion of the fuse-wire.

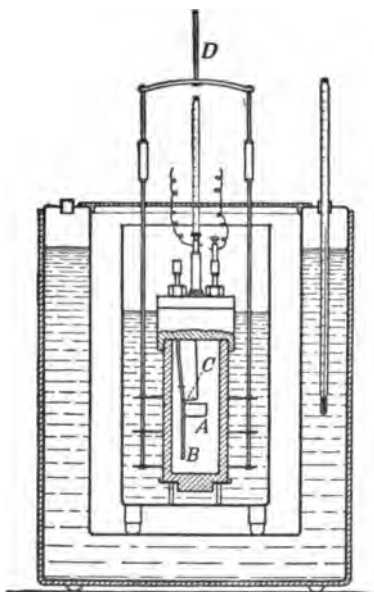


FIG. 141

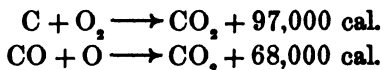
**General laws.** In interpreting the results of such measurements and in calculating the heat of other reactions from data collected in this way two general theorems are of constant application.

1. *Heat of formation of a substance equal to its heat of decomposition.* By the heat of formation of a substance is meant the heat evolved or absorbed in the formation of a gram-molecular

*weight from its elements.* Save in the case of rather simple substances it is not possible to determine the heat of formation directly. By decomposing a substance in various ways and determining the heat changes taking place, it is often possible to calculate the heat of formation on the assumption that it is equal to the heat of decomposition. This is, of course, a special application of the law of conservation of energy.

2. *The law of heat summation; the law of Hess.* As early as 1840 Hess worked out the general theorem that *the heat given off in a series of transformations is independent of the several steps, and depends only upon the initial and final states of the substance.* For example, carbon may be burned first to carbon monoxide, and this in turn to the dioxide. The sum of the heats in the two stages is the same as if the carbon were to be burned directly to the dioxide. This principle is of constant application in calculating some step in the series which cannot be directly measured.

For example, the heat of formation of carbon monoxide cannot be directly determined, but may be calculated from the equations



The difference between these two equations gives us the following:

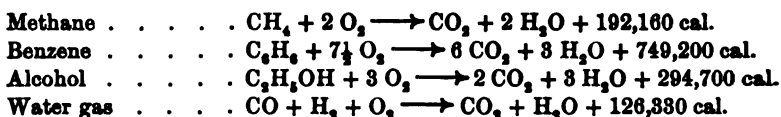


This law is also a special application of the law of conservation of energy, but was formulated before the more general law was well recognized.

**Types of heat measurements.** The general scope of heat measurements may be indicated by discussing a number of typical cases.

1. *Heat of combustion.* One of the most important determinations is that of the heat evolved when a substance is burned to its ultimate oxidation products. Such measurements are of the greatest technical importance as well as of much theoretical

value. As examples we have the following (assuming that the water remains as vapor):



**Fuels.** The various materials used as fuels differ much in the heat which they give out when burned. While many other factors are concerned in the value of a fuel, the chief one is its heat of combustion. The heat evolved by the combustion of one gram of a fuel is called its *calorific value*. Sometimes the heat value is expressed in *British thermal units* (B.T.U.), in which case the unit is the heat required to raise 1 pound of water 1° Fahrenheit (= 252 cal.). In large contracts the price paid for a fuel is generally based on its calorific value, as well as upon its adaptability to the use to which it is to be put. The following table will give some average values for a few common fuels:

#### CALORIFIC VALUES OF FUELS

Wood (air-dried)	about 3800–4000 cal.
Lignite (brown), 8% ash, 12% moisture	about 5400 cal.
Bituminous coal (Pennsylvania), 35% volatile matter, 6% ash	about 8300 cal.
Bituminous coal (Pocahontas), 18% volatile matter, 6% ash	about 8700 cal.
Anthracite coal (Connellsville), 12% ash	about 7300 cal.
Coke, 10% ash	about 7800 cal.

**Foods.** One of the most important functions of food is to supply the energy expended by the body. Apart from mineral salts and water, most of the constituents of foods which are digested ultimately undergo oxidation in the body, the carbon and hydrogen being in large part oxidized into carbon dioxide and water. The heat of the body is due to this oxidation. The chief function of a considerable portion of our food is to maintain this supply of energy, so the calorific value of foods is a matter of much importance. It is estimated by Sherman that

a man of average size, living a normal professional life involving no manual labor, requires the supply of from 2,000,000 to 2,250,000 cal. daily.

On the average the calorific values of the three principal groups of foodstuffs, as determined in the calorimeter and in actual combustion within the body, are as follows:

	CALORIMETER	BODY COMBUSTION
Carbohydrates . . . . .	4100 cal.	4000 cal.
Fats . . . . .	9450 cal.	9000 cal.
Proteins . . . . .	5650 cal.	4000 cal.

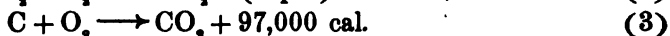
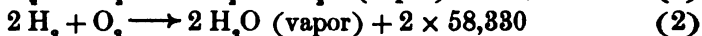
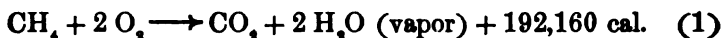
The following table, also taken from Sherman, shows the weight in grams of a few important foods required to yield 100,000 cal.

Beef, free from visible fat . . . . . 86 g.	Butter . . . . . 14 g.
Beef, round steak . . . . . 64 g.	Bread (white). . . . . 38 g.
Bacon, smoked . . . . . 19 g.	Sugar . . . . . 25 g.
Eggs . . . . . 67 g.	Potatoes . . . . . 120 g.
Milk . . . . . 145 g.	Beans (dried) . . . . . 29 g.

**2. Heat of formation.** Knowledge as to the heat of formation of a substance is often of the greatest service in forecasting its probable conduct toward various reagents. If this heat is great, the substance is likely to be indifferent toward decomposing reagents, or to act upon them only at high temperatures. Thus the heat of formation of carbon dioxide is 97,000 cal. This large heat value would indicate that only those substances which have a very strong affinity for oxygen will be able to reduce the oxide.

In the case of some simple substances the heat of formation can be determined directly, as in the case of carbon dioxide and of sulfur dioxide. In the majority of cases, however, the value must be calculated from measurements on the heat of combustion. For example, it is not possible to prepare methane from its elements under conditions which permit of measuring

directly its heat of formation. This can be calculated from the following equations:

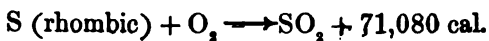


By adding equations (2) and (3) we get 213,660 cal. as the heat evolved in the formation of  $2 \text{H}_2\text{O} + \text{CO}_2$  from the elements, as against 192,160 cal. when formed by the combustion of methane. Consequently,  $213,660 - 192,160 \text{ cal.} = 21,500 \text{ cal.}$  must be evolved when methane is formed from carbon and hydrogen; in other words, *the heat of formation of methane is 21,500 cal.*

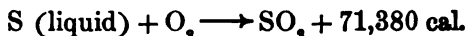
**8. Heat of solution.** When a substance dissolves in water, there is always a change in the temperature of the water, indicating either a heat evolution or absorption in the process of solution. *This change is the algebraic sum of a number of separate effects.* A solid or a gas after solution is, in a sense, in the state of a liquid, so that there is an effect corresponding in a general way to the heat of fusion or of liquefaction. There is usually a change in volume, involving mechanical work. If the solute is an electrolyte, ionization takes place, and this, like all chemical actions, involves heat changes, which may be either positive or negative. Undoubtedly many solutes combine chemically with the water, forming hydrates.

It is not possible to analyze the total heat change into the fractions to be assigned to each of these causes, but the total effect is of much importance, since it must be applied as a correction in many measurements in which the reaction takes place in solution.

**Corrections for concurrent physical changes.** It frequently happens that changes in state or crystalline form accompany chemical reactions, and to quite an extent these modify the total heat change in the reaction. For example, when solid rhombic sulfur is burned, we have the equation



When liquid sulfur is burned, the equation is



The difference, 300 cal., represents the heat of fusion of the sulfur.

In like manner, when oxygen and hydrogen combine to form *steam at 100°*, the equation is



If the heat is measured under such conditions that the resulting water is *liquid at 20°*, the equation becomes



If a gas is formed during a reaction, and is allowed to expand against the pressure of the atmosphere, it evidently performs work, and this is at the expense of the heat given off in the reaction. Since 1 gram-molecule of all gases occupy the same volume at atmospheric pressure (22.4 l.), the heat absorbed by the free expansion of all gases will be the same for each gram-molecule formed. This has been found to amount to 600 cal. at room temperature (27°).

For example, if carbon is burned in open air we have

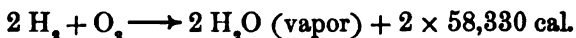


If burned in a bomb, the equation is



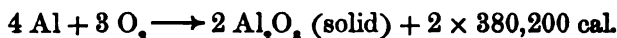
**Limits of temperature in combustion.** To secure a very high temperature by a chemical reaction it would seem that all we need to do is to bring as much material into reaction as we can in the briefest time possible, while in every way we guard against loss of heat by conduction. Since in this way we can liberate as much heat as we choose, there would seem to be no limit to the temperature we might hope to attain. But by experiment we find that this is not always true.

For example, we can burn hydrogen according to the equation



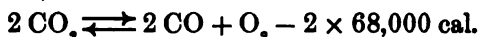
and so, for every 4 g. of hydrogen burned, liberate a very large amount of heat. Yet we find that we cannot attain a temperature much higher than will suffice to melt platinum — say 2000°.

If we burn aluminium we have the equation



which shows that *for every gram burned* we get much less heat than in the case of hydrogen, yet we can get a temperature estimated to be as high as 4000°.

The explanation of this seeming contradiction lies in the *properties of the compound formed* in the reaction. When we approach about 2000° water begins to dissociate into hydrogen and oxygen (p. 76) and in so doing absorbs heat. This reverse reaction presently absorbs as much heat as is liberated by the direct reaction (p. 289), and heat equilibrium results with no further rise in temperature. In the combustion of carbon the case is similar, the equilibrium being expressed in the equation



With aluminium the product of combustion ( $\text{Al}_2\text{O}_3$ ) is stable up to the extreme limit of experiment, and all the heat of combination is available to raise the temperature of the resulting aluminium oxide and surrounding bodies.

The determining factor in the temperature which can be secured by a given reaction is therefore not only the heat of reaction but also the stability of the reaction product at high temperatures.

**Conditions for stability of exothermic and endothermic compounds.** The dissociation of the strongly exothermic compounds, water and carbon dioxide, at high temperatures is in accord with the principle of Le Chatelier (p. 290), which predicts that a heat-absorbing reaction will tend to take place as the temperature is raised. It has been found to be true in general that exothermic compounds tend to dissociate in a similar way at high temperatures, and, conversely, that they become more stable as the

temperature is lowered. In view of the large heat evolution attending the formation of aluminium oxide, we should expect it to dissociate when heated sufficiently, and it doubtless would do so if we could reach the necessary temperature.

On the other hand, the principle of Le Chatelier would lead us to expect that an endothermic compound would tend to form from its elements at a high temperature, but would become unstable at lower temperatures, dissociating with heat evolution. This is found to be the case. For example, carbon and hydrogen readily combine at the temperature of the electric arc to form acetylene, and this compound becomes more and more unstable as the temperature is lowered. It is easy to see that if this world was once in gaseous condition, the first compounds to form must have been endothermic in character.

### QUESTIONS

1. If we burn alcohol in a bomb calorimeter measuring the heat evolution at  $20^{\circ}$ , and then wish to calculate the heat that would have been evolved if the combustion had occurred in the open air, the gaseous products reaching a final temperature of  $200^{\circ}$ , how many factors can you think of that would require thermal corrections?

2. How do you account for the high heat of combustion of acetylene, namely 301,630 cal.? What other compounds can you name that should have high heats of combustion?

3. In view of the highly explosive nature of nitroglycerine, what would you expect as to its heat of formation?

4. Aside from the heat of chemical reaction, what heat-absorbing or evolving transformations are involved in converting carbon into carbon dioxide?

5. Can you see any reason for the small heat of formation of the *gaseous* hydrocarbons, especially in view of the fact that they are quite stable compounds?

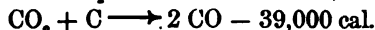
6. Account for the fact that the heat of combustion of gaseous alcohol ( $C_2H_5OH$ ), namely 305,400 cal., is greater than that of alcohol in the liquid state? Also, why is it less than that of the corresponding gaseous hydrocarbon ethane ( $C_2H_6$ ) which is 340,300 cal.?

7. How would a thermos bottle serve as a calorimeter?

## PROBLEMS

1. Calculate the calorific value (per gram) of aluminium and of hydrogen.

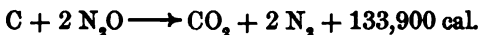
2. Refer to the two equations (pp. 429, 419):



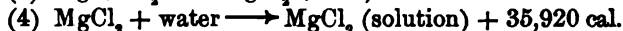
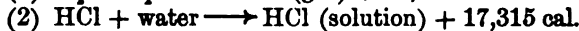
In what volume proportions must the two gases  $\text{CO}_2$  and  $\text{O}_2$  be passed over hot carbon to avoid any loss or gain of heat?

3. Calculate the heat of formation of formic acid ( $\text{CH}_2\text{O}_2$ ) from its elements, its heat of combustion being 65,900 cal.

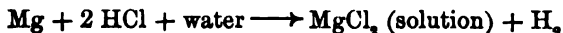
4. Calculate the heat of formation of  $\text{N}_2\text{O}$  from the equations



5. Given the equations:



Calculate the heat of the reaction:



## CHAPTER XXVIII

### CARBOHYDRATES; ALCOHOLS; ORGANIC ACIDS AND THEIR DERIVATIVES

**Carbohydrates.** The term *carbohydrate* is applied to a class of compounds which includes the sugars, starch, and allied substances. These compounds contain carbon, hydrogen, and oxygen, the last two elements usually being present in the proportion in which they combine to form water; hence the term *carbohydrates*. The most important carbohydrates are the following:

TABLE OF CARBOHYDRATES

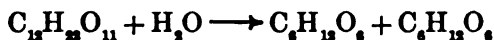
Sucrose (ordinary sugar) . . . . .	$C_{12}H_{22}O_{11}$
Lactose (milk sugar) . . . . .	$C_{12}H_{22}O_{11} \cdot H_2O$
Maltose . . . . .	$C_{12}H_{22}O_{11} \cdot H_2O$
Dextrose (grape sugar) . . . . .	$C_6H_{12}O_6$
Levulose . . . . .	$C_6H_{12}O_6$
Cellulose . . . . .	$(C_6H_{10}O_5)_x$
Starch . . . . .	$(C_6H_{10}O_5)_x$

The molecular formulas of cellulose and starch are unknown, but are multiples of the simple formula  $C_6H_{10}O_5$ ; accordingly they are often written  $(C_6H_{10}O_5)_x$ . In the discussions of the compounds they will be represented by the simple formula  $C_6H_{10}O_5$ .

**Sucrose (sugar) ( $C_{12}H_{22}O_{11}$ ).** This substance, ordinarily called *sugar*, occurs in many plants, especially in the sugar cane and sugar beet. The sugar cane grows only in warm climates (Cuba and the Hawaiian Islands are the greatest producers), while the sugar beet thrives in cooler climates, such as prevail in Ohio and Michigan in the United States, and in Germany. The beets contain as high as 16 per cent of sucrose.

**The manufacture of sugar.** The juice from the cane or beet contains the sugar in solution along with many impurities. These impurities are removed by appropriate methods, and the resulting solution is then evaporated until the sugar crystallizes. The evaporation is conducted in closed vessels from which the air is partially exhausted (vacuum pans). In this way the boiling point of the solution is lowered and the charring of the sugar is prevented. It is not practicable to remove all the sugar from the solution. Ordinary *molasses* is the solution which remains after a part of the sugar has been crystallized out from the purified juice of the sugar cane. The sweetness of maple sugar is due to sucrose, other products present in the maple sap imparting the distinctive flavor. The annual consumption of sugar in the United States amounts to approximately 90 lb. for each person.

**Chemical conduct of sugar.** When a solution of cane sugar is heated to about 70° with hydrochloric acid, two isomeric sugars, *dextrose* and *levulose*, are formed in accordance with the following equation:



In this process the sugar is said to be *inverted*, and the mixture of dextrose and levulose is termed *invert sugar*.

When heated to 160°, sucrose melts; if the temperature is increased to 200°, a partial decomposition takes place and a brown substance, known as *caramel*, forms. This is used in making confectionery and as a coloring matter in certain foods.

**Lactose (milk sugar)** ( $\text{C}_{12}\text{H}_{22}\text{O}_{11} \cdot \text{H}_2\text{O}$ ) This compound is present in the milk of all mammals. The average composition of cow's milk is as follows:

Water . . . . .	87.17%
Casein (nitrogenous matter) . . . . .	3.56%
Butter fat . . . . .	3.64%
Lactose . . . . .	4.88%
Mineral matter . . . . .	0.75%

When *rennin* (a substance obtained from the stomach of calves) is added to milk, the casein separates. This is the part of the milk used in the manufacture of *cheese*. The liquid remaining after the separation of the casein is known as *whey*. This contains the milk sugar, which crystallizes on evaporation; it resembles sucrose in appearance, but is not so sweet nor so soluble. The souring of milk is due to the fact that the milk

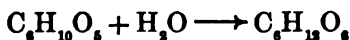
sugar contained in it changes into *lactic acid*, a liquid having the formula  $C_3H_5O_3$ :



This change is brought about by a certain microorganism which enters from the air, and the process is known as *lactic fermentation*.

**Maltose** ( $C_{12}H_{22}O_{11} \cdot H_2O$ ). This sugar resembles sucrose and lactose in its general properties. It is prepared by the action of malt upon starch; hence the name *maltose*. Malt is the name applied to barley which has been moistened, kept in a warm place until it has germinated, and then heated until the vitality of the grain has been destroyed. In the process of germination a substance is formed known as *diastase*, and it is this substance which imparts to malt its property of changing starch into maltose.

**Dextrose** (grape sugar, glucose) ( $C_6H_{12}O_6$ ). This sugar is present in honey and in many fruits. It is usually associated with levulose, and is often called *grape sugar* because of its presence in grape juice. It can be obtained along with levulose by heating sucrose with hydrochloric acid. Commercially it is prepared in enormous quantities by heating starch with small amounts of hydrochloric acid, which acts as a catalytic agent. The starch is first changed into a sweet-tasting solid known as *dextrin*, and this, on further action, is converted into dextrose:



When the change is complete the hydrochloric acid is neutralized by sodium carbonate.

Pure dextrose is a white crystalline solid resembling sucrose in its properties, but not so sweet. Most of the dextrose used is in the form known commercially as *glucose*, or *corn sirup*. This is a thick sirupy liquid and consists of an aqueous solution of dextrin, dextrose, and maltose. Large quantities of glucose are used in the preparation of jellies, jams, sirups, candy, and other sweets. A federal ruling requires that when glucose is present in such foods as jellies and jams, the label on the container must state the percentage of glucose present.

**Levulose (fruit sugar) ( $C_6H_{12}O_6$ ).** Levulose is a white solid which occurs along with dextrose in fruits and honey. It is sweet and has the general properties of a sugar.

**Starch ( $C_6H_{10}O_5$ ).** This compound is one of the most abundant carbohydrates found in nature, being present especially in seeds and tubers. In the United States it is obtained chiefly from corn, about 60 per cent of which is starch. In Europe it is obtained principally from the potato. Starch consists of minute granules. These granules are composed of a substance known as granulose, surrounded by a membrane composed principally of cellulose. The granulose is soluble in water. Starch does not dissolve



FIG. 142. Cornstarch  
Magnified 260 diameters

in cold water, however, since the granulose is protected from the action of water by the insoluble cellulose membrane. When heated with water, the membranes burst and the granulose dissolves. Starch granules differ from each other somewhat in appearance, according to the source of the starch, so that it is generally possible to determine the origin of any particular sample by its microscopic appearance. Figs. 142 and 143 represent the appearance of typical granules of starch derived from corn and wheat, when viewed under the microscope.

**Cellulose ( $C_6H_{10}O_5$ ).** Cellulose forms the basis of all woody fibers. Cotton and linen are nearly pure cellulose. It is insoluble in water, alcohol, or dilute acids, but will dissolve in a solution prepared by dissolving copper oxide in ammonium hydroxide. Concentrated hydrochloric acid changes it into dextrose. A mixture of concentrated nitric and sulfuric acids forms compounds which are known as *nitrocellulose*, or *guncotton*. These are very inflammable and under certain conditions are highly explosive.



FIG. 143. Wheat starch  
Magnified 260 diameters

They form the principal constituent of most *smokeless powders*. Photographic films are also made from them, as well as from a noninflammable derivative of cellulose known as *cellulose acetate*. A solution of the acetate is used in covering the cloth employed in the construction of *aëroplanes*. *Collodion* is a solution of certain nitrocelluloses in a mixture of alcohol and ether. Nitrocellulose and camphor when mixed together form a plastic jelly which gradually hardens, forming the material known as *celluloid*. This is used for making such objects as combs and brush handles. Celluloid is easily inflammable, and care should be exercised in the use of celluloid articles.

**Characteristics of various textile fibers.** Of the different fibers used in making the yarns from which the common fabrics are prepared, the vegetable fibers, cotton and linen, are essentially cellulose, while the animal



FIG. 144

fibers, wool and silk, are composed of nitrogenous substances. Although these fibers resemble each other when viewed with the naked eye, their appearance is distinctive when examined with the microscope. The characteristic appearance of these fibers is shown in Fig. 144. It is also possible to distinguish between the fibers by the action of chemical reagents. For example, a hot solution of sodium hydroxide (5 per cent to 10 per cent) has but little action upon cotton, while it will readily dissolve wool and slowly dissolve silk.

**Paper.** Paper consists mainly of cellulose. The finer grades are made from linen and cotton rags, and the cheaper grades from wood.

**Manufacture of paper.** In making paper the raw material is cut into pieces and treated with suitable reagents (calcium acid sulfite is used in case of wood), to remove all objectionable matter, leaving the cellulose,

which is then bleached with chlorine. The paper pulp so obtained is suspended in water and run onto wire screens. It then passes between large iron cylinders, some of which are heated with steam. In this way the pulp is pressed and dried and delivered in the form of paper. In the process different materials are often added to the pulp. These vary with the nature of the paper desired; thus, finely ground clay or calcium sulfate is added to give body to the paper. In making paper intended for writing or printing, a compound prepared by heating resin and sodium hydroxide is added, together with aluminium sulfate. This makes a finished surface and prevents the ink from spreading.

**Alcohols.** The *alcohols* may be regarded as derived from the hydrocarbons by substituting for one or more hydrogen atoms a corresponding number of hydroxyl groups. A great many alcohols are known, and, like the hydrocarbons, they may be arranged in series. The relation between the first three members of the methane series and the corresponding alcohols is shown in the following table:

$\text{CH}_4$ (methane)	. . . . .	$\text{CH}_3\text{OH}$ (methyl alcohol)
$\text{C}_2\text{H}_6$ (ethane)	. . . . .	$\text{C}_2\text{H}_5\text{OH}$ (ethyl alcohol)
$\text{C}_3\text{H}_8$ (propane)	. . . . .	$\text{C}_3\text{H}_7\text{OH}$ (propyl alcohol)

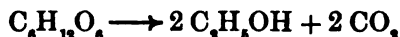
The terms *methyl*, *ethyl*, and *propyl*, used in designating the different alcohols, are names applied to the univalent radicals  $\text{CH}_3$ ,  $\text{C}_2\text{H}_5$ , and  $\text{C}_3\text{H}_7$ , respectively. It will be noted that the names of these radicals are derived from the names of the corresponding hydrocarbons by changing the ending *-ane* to *-yl*.

**Methyl alcohol (wood alcohol) ( $\text{CH}_3\text{OH}$ ).** This compound is obtained in the destructive distillation of wood, and on this account is called wood alcohol. It is a colorless liquid which has a density of 0.79 and boils at about  $66^\circ$ . It burns with an almost colorless flame and is sometimes used for heating purposes. It is a good solvent for organic substances and is used to a considerable extent as a solvent in the manufacture of varnishes. Its chief use is in the manufacture of formaldehyde (p. 451). *It is very poisonous.* It has a specific action upon the optic nerve, and many cases of blindness have resulted both from drinking the liquid and from repeatedly inhaling its vapor.

Duncan states that "out of ten men who drink 4 oz. of pure methyl alcohol in any form whatever, four will probably die, two of them becoming blind before death. The remaining six may recover, but of these, two will probably be permanently blind."

**Ethyl alcohol ( $C_2H_5OH$ ).** This is the compound commonly designated as *alcohol*.

1. **Preparation.** It is prepared by the action of ordinary brewers' yeast upon certain sugars, especially maltose and dextrose. With dextrose the reaction is expressed by the following equation:



This process, in which a sugar is changed into alcohol and carbon dioxide by the action of yeast, is known as *alcoholic fermentation*. The yeast is a low form of plant life which grows in the sugar solution under suitable conditions. During its growth it secretes a substance known as *zymase*, which is the active agent in effecting alcoholic fermentation. While sucrose does not ferment directly, the addition of yeast to its aqueous solution first resolves the sucrose into dextrose and levulose, both of which then ferment.

**Laboratory preparation of alcohol.** The formation of alcohol and carbon dioxide from dextrose may be shown as follows: About 100 g. of dextrose is dis-

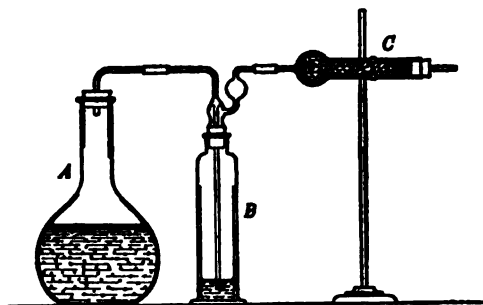
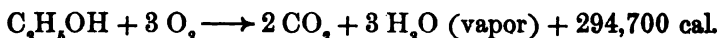


FIG. 145

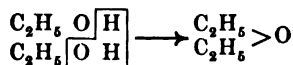
solved in a liter of water in the flask A (Fig. 145). This flask is connected with the bottle B, which is partially filled with limewater. The tube C contains solid sodium hydroxide. A little bakers' yeast is now added to the solution in flask A, and the apparatus is connected as shown in the figure. If the temperature is maintained at  $30^\circ$ , the reaction soon begins. Bubbles of gas escape through the limewater in B. A precipitate of calcium carbonate soon forms, showing the presence of carbon dioxide. The guard tube C prevents access of carbon dioxide from the air. The alcohol remains in the flask A and may be separated by fractional distillation.

Commercially, alcohol is prepared either from crude molasses which is shipped to the United States from Cuba in large quantities for this purpose, or from starch obtained chiefly from corn and potatoes. When starch is used, it is first converted into maltose by the action of malt, the maltose being then changed into alcohol and carbon dioxide by yeast. Whether prepared from the sugar present in the molasses or from maltose, it is possible to obtain by direct fermentation an aqueous solution containing from 15 to 20 per cent of alcohol. By fractional distillation this may be concentrated to a solution containing 96 per cent of alcohol. When lime ( $\text{CaO}$ ) is added to this solution, and the mixture heated, most of the remaining water combines with the lime to form calcium hydroxide. Upon distilling the resulting mixture, alcohol containing less than 1 per cent of water distills over. Such alcohol is termed *absolute alcohol*. The ordinary alcohol of the druggist contains approximately 95 per cent by volume of alcohol.

2. **Properties.** Ethyl alcohol is a colorless liquid with a pleasant odor and different from that of methyl alcohol. It has a density of 0.789 at  $20^\circ$ , boils at  $78.30^\circ$ , and solidifies at  $-112.3^\circ$ . It resembles methyl alcohol in its general properties. When ignited it burns with a hot flame:



It is sometimes used as a source of heat, since it does not deposit carbon, as does the flame from oils. When taken into the system in small quantities it causes intoxication; in larger quantities it acts as a poison. The intoxicating properties of such liquors as beer, wine, and whisky are due to the alcohol present. When heated to  $140^\circ$  with sulfuric acid it loses the elements of water, forming ordinary ether, as shown in the following equation:

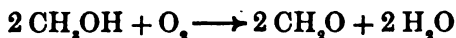


Ether is a colorless liquid boiling at  $35^\circ$  and is largely used as an anesthetic in surgical operations.

**Denatured alcohol.** The Federal government imposes a heavy tax on alcohol (as well as on such alcoholic liquors as are allowed to be sold), the exact amount of the tax depending upon the amount of alcohol present. The tax on the ordinary 95% alcohol previous to the war was \$2.10 per gallon; since the war it has been doubled, amounting to about \$4.20 per gallon. The prohibition act limits the sale of alcohol to a few very definite uses. It can be obtained, tax free, by educational institutions, to be used for scientific purposes. For commercial purposes, *denatured alcohol* is used, and this is also tax free. Denatured alcohol is alcohol to which has been added a definite amount of some substance which renders it unfit for beverage purposes but which does not impair its use for manufacturing purposes. The substances which may be used for this purpose are prescribed by law, and are known as *denaturants*. The most common denaturant is the vile-smelling compound known as pyridine (p. 141).

**Alcoholic liquors.** All alcoholic liquors are made by alcoholic fermentation. Wine is made by the fermentation of the dextrose in grape juice and contains from 5 to 15 per cent by volume of alcohol. Beer is made from maltose, formed by the action of malt upon starch obtained from various grains, chiefly barley. It contains from 3 to 5 per cent by volume of alcohol. Whisky contains about 50 per cent by volume of alcohol, and is made from starch by a process very similar to that described under the commercial preparation of alcohol. Almost any saccharine liquid, such as cider and the juices of fruits in general, gradually undergoes alcoholic fermentation when exposed to air, the yeast cells entering from the air.

**Aldehydes.** When treated with suitable oxidizing agents, alcohols are converted, by loss of hydrogen, into compounds known as *aldehydes*. The most important aldehyde is formaldehyde ( $\text{CH}_2\text{O}$ ), which is prepared by the oxidation of methyl alcohol:



Formaldehyde is a gas and is largely used as a disinfectant. An aqueous solution containing 40 per cent by weight of the gas is sold by druggists under the name *formalin*. When oxidized, formaldehyde yields formic acid ( $\text{CH}_2\text{O}_2$ ).

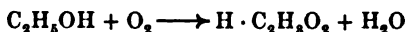
**Organic acids.** Like the other classes of organic compounds, the organic acids may be arranged in homologous series. One of the most important of these series is the *fatty-acid series*, so called because the derivatives of certain of its members are constituents of the fats. Some of the most important members of the series are given in the following table. They are all mono-basic, and this fact is expressed in the formulas by separating the replaceable hydrogen atom from the rest of the molecule :

$\text{H} \cdot \text{CHO}_2$ . . . . .	formic acid, a liquid boiling at $100^{\circ}$ – $101^{\circ}$
$\text{H} \cdot \text{C}_2\text{H}_3\text{O}_2$ . . . . .	acetic acid, a liquid boiling at $118^{\circ}$
$\text{H} \cdot \text{C}_3\text{H}_5\text{O}_2$ . . . . .	propionic acid, a liquid boiling at $140^{\circ}$
$\text{H} \cdot \text{C}_4\text{H}_7\text{O}_2$ . . . . .	butyric acid, a liquid boiling at $163^{\circ}$
$\text{H} \cdot \text{C}_{16}\text{H}_{31}\text{O}_2$ . . . . .	palmitic acid, a solid melting at $62^{\circ}$
$\text{H} \cdot \text{C}_{18}\text{H}_{35}\text{O}_2$ . . . . .	stearic acid, a solid melting at $69^{\circ}$
General formula $\text{H} \cdot \text{C}_n\text{H}_{2n-1}\text{O}_2$	

**Formic acid ( $\text{H} \cdot \text{CHO}_2$ ).** This is a colorless liquid and occurs in many plants, such as the stinging nettle. It is also present in a certain species of ant; hence the name *formic acid*, the word *formic* being derived from a Latin word meaning "ant."

**Acetic acid ( $\text{H} \cdot \text{C}_2\text{H}_3\text{O}_2$ ).** This is best known as the acid which imparts the sour taste to vinegar. It is prepared commercially by the destructive distillation of wood (p. 139). It is a colorless liquid and has a strong, pungent odor. When anhydrous, it crystallizes as a white solid which melts at  $18^{\circ}$ , and closely resembles ice in appearance; hence the name *glacial* acetic acid. Many of the salts of acetic acid are well-known compounds. Thus lead acetate ( $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3 \text{H}_2\text{O}$ ) is the white solid known as *sugar of lead*.

**Vinegar.** All vinegars are prepared by the action of the vegetable organism known as *Mycoderma aceti* (present in the so-called "mother of vinegar") upon a liquid containing alcohol. This change of alcohol into acetic acid through the action of the organism is known as *acetic fermentation*, and may be expressed by the following equation :



Instead of starting with the alcoholic liquid one may use some substance which contains starch or sugar, such as barley, cider, or molasses. In such

cases the starch and sugar present are first converted into alcohol, as explained under the preparation of alcohol. Thus, in the manufacture of cider vinegar the sugar in the apple juice first undergoes alcoholic fermentation, the alcohol formed then undergoing acetic fermentation.

**Butyric acid ( $H \cdot C_4H_7O_2$ ).** Butyric acid is a liquid of disagreeable odor. A derivative of the acid is present in butter and gives it its characteristic taste.

**Palmitic and stearic acids.** These are white solids insoluble in water. They are obtained from fats.

**Relation between the hydrocarbons, alcohols, aldehydes, and acids.** The statement has been made that the alcohols may be regarded as derived from the hydrocarbons by the substitution of a hydroxyl group for hydrogen; also, that the alcohols, when oxidized, yield aldehydes by loss of hydrogen, and that the aldehydes on further oxidation are changed into acids. The relation between these compounds may be seen from the following formulas, representing methane and ethane and the corresponding alcohols, aldehydes, and acids:

$CH_4$ (methane)	$CH_3OH$ (methyl alcohol)	$CH_2O$ (formaldehyde)	$CH_2O_2$ (formic acid)
$C_2H_6$ (ethane)	$C_2H_5OH$ (ethyl alcohol)	$C_2H_4O$ (acetaldehyde)	$C_2H_4O_2$ (acetic acid)

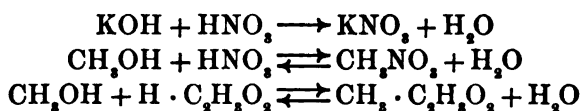
**Acids belonging to other series.** In addition to the members of the series described above, mention may be made of the following well-known acids, the first four of which are white solids:

1. **Oxalic acid ( $H_2C_2O_4 \cdot 2H_2O$ )** is found in many plants.
2. **Malic acid ( $H_2 \cdot C_4H_4O_6 \cdot H_2O$ )** occurs in a free state in apples, pears, and other fruits, as well as in the berries of the mountain ash.
3. **Tartaric acid ( $H_2 \cdot C_4H_4O_6$ )** occurs in many fruits, especially the grape, either in a free state or in the form of its salts. Some of its salts are well-known compounds. The potassium acid tartrate ( $KHC_4H_4O_6$ ) is ordinarily known as *cream of tartar*. It is a white solid obtained from grape juice in the manufacture of wine, and is used in the manufacture of baking powders. Potassium sodium tartrate ( $KNaC_4H_4O_6 \cdot 4H_2O$ ) is used in medicine under the name *Rochelle salt*.
4. **Citric acid ( $H_2 \cdot C_6H_8O_7 \cdot H_2O$ )** occurs especially in lemons.

5. **Lactic acid** ( $H \cdot C_3H_5O_2$ ) is a liquid formed from lactose in the souring of milk. The formation of lactic acid from lactose is known as *lactic fermentation*; like alcoholic and acetic fermentation, it is caused by the presence of a low form of vegetable organism.

6. **Oleic acid** ( $H \cdot C_{18}H_{35}O_2$ ) is an oily liquid. Certain derivatives of oleic acid constitute the principal part of many oils and fats.

**Esters, oils, and fats.** When acids are mixed with alcohols under certain conditions, a reaction occurs similar to that which takes place between acids and bases. The following equations will serve as illustrations:



The resulting compounds, of which methyl acetate ( $CH_3C_2H_5O_2$ ) may be taken as an example, are known as *esters*. They differ from ordinary salts in that they contain a hydrocarbon radical, such as  $CH_3$  or  $C_2H_5$ , in place of a metal.

The fats are largely mixtures of the esters known as *olein*, *palmitin*, and *stearin*. These esters may be regarded as derived from oleic, palmitic, and stearic acids respectively by replacing the hydrogen of the acid with the glycerin radical  $C_3H_5$ . This radical is tervalent, and since oleic, palmitic, and stearic acids contain only one replaceable hydrogen atom to the molecule, it is evident that three molecules of each acid must enter into the formation of each molecule of the ester. The formulas for the acids and the esters derived from each are as follows:

ACIDS	ESTERS
$H \cdot C_{18}H_{35}O_2$ (oleic acid)	$C_3H_5(C_{18}H_{35}O_2)_3$ (olein)
$H \cdot C_{16}H_{31}O_2$ (palmitic acid)	$C_3H_5(C_{16}H_{31}O_2)_3$ (palmitin)
$H \cdot C_{18}H_{35}O_2$ (stearic acid)	$C_3H_5(C_{18}H_{35}O_2)_3$ (stearin)

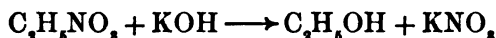
Olein is a liquid, while palmitin and stearin are solids. The oils are mainly olein, while the solid fats are mainly palmitin and stearin.

**Butter fat and oleomargarine.** While butter fat, like other fats, consists principally of olein, palmitin, and stearin, its characteristic flavor is due to the presence of a small amount (about 8 per cent) of the fat *butyrin*, which is an ester of butyric acid and has the formula  $C_3H_7(C_4H_7O_2)_3$ . Oleomargarine differs from butter mainly in the fact that a smaller amount of butyrin is present. It is made from the fats obtained from cattle and hogs. Sometimes cottonseed oil and coconut oil are also added. These fats are churned with milk or mixed with a small amount of butter, in order to furnish sufficient butyrin to give the butter flavor.

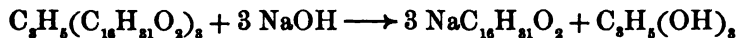
In appearance oleomargarine differs from most butter in being nearly colorless. While it is a common practice to color butter artificially, the Federal law permits the coloring of oleomargarine only upon the payment of a tax of 10 cents for each pound colored. Many of the states, however, have laws forbidding the sale of oleomargarine that is artificially colored, even though the federal tax has been paid.

**Changing oils into solid fats.** It will be noted that stearin differs from olein in composition in that it contains six more atoms of hydrogen in each molecule. Now if hydrogen is brought in contact with olein under proper conditions and in the presence of a suitable catalytic agent (finely divided nickel is used), the olein takes up the additional hydrogen and is changed into the solid stearin. It is possible in this way to change the oils into solid fats. Certain commercial fats used in cooking are made by this process from the comparatively inexpensive cottonseed oil.

**Saponification; soaps.** When an ester such as ethyl nitrate ( $C_2H_5NO_3$ ) is heated with an alkali, a reaction expressed by the following equation takes place:



This type of reaction is known as *saponification*, since it is the one which takes place in the manufacture of soaps. The ordinary soaps are made by heating fats with a solution of sodium hydroxide. The reactions involved may be illustrated by the following equation representing the reaction between palmitin and sodium hydroxide:

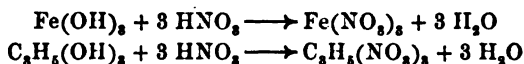


In accordance with this equation the esters which constitute the fats and oils are converted into the sodium salts of the corresponding acids and glycerin ( $C_3H_7(OH)_3$ ). The sodium salts are separated and constitute ordinary soaps. These salts are soluble in water. When added to water containing calcium salts,

the insoluble calcium palmitate and stearate are precipitated. Magnesium salts act in a similar way. It is because of these facts that so much soap is used up by hard water. The glycerin formed in the manufacture of soaps is recovered, and it is from this source that the glycerin of commerce is obtained.

**Glycerin ( $C_3H_8(OH)_3$ ).** This compound may be regarded as derived from propane ( $C_3H_8$ ) by replacing three atoms of hydrogen with three hydroxyl groups. It is therefore an alcohol. It is an oily, colorless liquid having a sweetish taste. Glycerin is used in medicine and in the manufacture of nitroglycerin and dynamite.

**Nitroglycerin and dynamite.** Nitric acid reacts with glycerin in the same way that it reacts with any base containing three hydroxyl-groups, such as  $Fe(OH)_3$ :



The resulting nitrate,  $C_3H_5(NO_3)_3$ , is the main constituent of nitroglycerin, a slightly yellowish oil characterized by its explosive properties. It explodes by pressure, by detonation, or by heating to  $250^\circ$ . The following equation represents in a general way the changes which take place in the decomposition of nitroglycerin:



One volume of nitroglycerin on explosion yields about 1300 volumes of gaseous compounds, which are expanded by the heat of explosion to over 10,000 volumes. Dynamite consists of a mixture of sodium nitrate, or ammonium nitrate, wood pulp, and nitroglycerin. The wood pulp acts as an absorbent for the nitroglycerin. The strength of the dynamite depends on the percentage of nitroglycerin present. Dynamite is used much more than nitroglycerin, since it does not explode so readily on percussion, and therefore can be transported with safety.

Nitroglycerin is too powerful an explosive to be used alone in guns. It is a constituent of certain explosives, however, that are so used. Thus the English smokeless powder known as *cordite* consists of nitroglycerin, guncotton, and a little vaseline.

**The proteins.** The term *protein* is applied to a large class of complex nitrogenous compounds which are everywhere abundant in animal and vegetable organisms and which constitute the principal part of the tissues of the living cell. The casein of milk, gluten

of flour, and albumin of egg will serve as examples of protein matter. The proteins all contain nitrogen, carbon, hydrogen, and oxygen, and some contain sulfur and phosphorus in addition.

**Foods.** While the compounds present in our foods are very numerous and often exceedingly complex, yet they may all be included in a few general classes, namely, *proteins, fats, carbohydrates, mineral matter, and water*. Since the mineral matter is left as a residue when the food is burned, it is listed as ash in reporting the analyses of foods.

In a general way it may be stated that the protein matter in our food serves to replace the worn-out tissues of our bodies, as well as to supply material for growth. The carbohydrates and fats are more or less interchangeable, since both are oxidized in the body and serve as a source of heat and muscular energy. The mineral matter supplies the material for building up the solid tissues of the body and has, in addition, other more complex functions. The protein matter may fulfill the same function as the fats and carbohydrates if the latter are lacking in our foods. Since the various constituents of our foods serve different purposes, it is evident that a proper mixture of these is essential to health.

The composition of the edible portion of a few typical foods is given in the following table, taken from Sherman's "Chemistry of Food and Nutrition."

	WATER (Per cent)	PROTEIN (Per cent)	FAT (Per cent)	CARBOHY- DRATES (Per cent)	ASH (Per cent)
Beef free from visible fat	73.8	22.1	2.9		1.2
Salmon . . . . .	64.6	21.2	12.8		1.4
Eggs . . . . .	73.7	14.8	10.5		1.0
Milk . . . . .	87.0	3.3	4.0	5.0	0.7
Butter . . . . .	11.0	1.0	85.0		3.0
Oatmeal . . . . .	7.3	16.1	7.2	67.6	1.9
Wheat flour . . . . .	11.9	13.3	1.5	72.7	0.6
Bread, white . . . . .	35.3	9.2	1.3	53.1	1.1
Beans, dried . . . . .	12.6	22.5	1.8	59.6	3.5
Potatoes . . . . .	78.3	2.2	0.1	18.4	1.0
Tomatoes . . . . .	94.3	0.9	0.4	3.9	0.5

## QUESTIONS

1. Give examples of isomeric compounds from among the carbohydrates.
2. (a) Name the different kinds of fermentation discussed and the products formed in each case. (b) What is the cause of each? (c) Suggest a method for preventing fermentation.
3. Give the changes involved in the manufacture of absolute alcohol from corn.
4. Suggest a method for obtaining alcohol from sawdust.
5. How could you distinguish between ethyl alcohol and wood alcohol? between starch and cellulose? between cane sugar and beet sugar?
6. Write the formulas for the following compounds: sodium formate, calcium acetate, aluminium stearate, calcium oxalate, magnesium citrate, sodium oleate.
7. (a) Write the formula for the ester formed when ethyl alcohol reacts with butyric acid. (b) What is the name of the ester so formed?
8. Considering soap as sodium stearate, write the equation for the reactions that take place when such a soap is brought in contact with a water containing calcium sulfate.

## PROBLEMS

1. What weight of dextrose is necessary to prepare 100 kg. of absolute alcohol (99%,  $C_2H_5OH$ ) upon the supposition that 95 per cent of the sugar undergoes fermentation?
2. Contrast the amount of heat generated by the combustion of equal weights of benzene and ethyl alcohol.
3. What weight of methyl alcohol is necessary for the preparation of 1 kg. of formalin, assuming that the yield is 90 per cent of the theoretical yield?
4. The Pure Food and Drugs Act requires that all vinegars must contain not less than 4 g. of acetic acid in 100 g. of vinegar. Calculate approximately the per cent of sugar that must be present in cider so that the vinegar formed from it may fulfill the law's requirement as to the acetic-acid content.
5. It required 40 cc. of a tenth-normal solution of sodium hydroxide to neutralize the acetic acid in 5 g. of vinegar. Does the vinegar meet the law's requirement as to acetic acid?

## CHAPTER XXIX

### THE PHOSPHORUS FAMILY

	ATOMIC WEIGHT	DENSITY OF SOLID	MELTING POINT	BOILING POINT
Nitrogen . . . . .	14.008	1.0265	— 210	— 195.7
Phosphorus . . . . .	31.04	1.83	44	287.0
Arsenic . . . . .	74.96	5.73	850	
Antimony . . . . .	120.2	6.70	630	1440.0
Bismuth . . . . .	208.0	9.80	271	1420.0

**The group.** The elements of Group V have a maximum valence of 5. The type element nitrogen is followed by a family consisting of phosphorus, arsenic, antimony, and bismuth. The acid-forming qualities, which are very strong in phosphorus, gradually decline with increasing atomic weight, until in bismuth they have almost entirely disappeared and are replaced by those of a pronounced metal. Along with this change in chemical conduct there is a more or less regular variation in all physical constants, as is indicated in the table.

The other family in the group, comprising vanadium, columbium, and tantalum, is not so well known. It will be convenient to describe them later on in connection with certain other rare elements.

**Compounds.** In general the elements of the family form compounds having similar composition, in which the elements are either trivalent or pentavalent, as is shown in the following table:

$\text{PH}_3$	$\text{PCl}_3$	$\text{PCl}_5$	$\text{P}_2\text{O}_3$	$\text{P}_2\text{O}_5$
$\text{AsH}_3$	$\text{AsCl}_3$	$\text{AsCl}_5$	$\text{As}_2\text{O}_3$	$\text{As}_2\text{O}_5$
$\text{SbH}_3$	$\text{SbCl}_3$	$\text{SbCl}_5$	$\text{Sb}_2\text{O}_3$	$\text{Sb}_2\text{O}_5$
	$\text{BiCl}_3$	$\text{BiCl}_5$	$\text{Bi}_2\text{O}_3$	$\text{Bi}_2\text{O}_5$

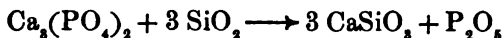
In the case of phosphorus, arsenic, and antimony the oxides are acid anhydrides. Salts of at least four acids of each of these three elements are known, the free acid in some instances being unstable. Nitrogen has been discussed in an earlier chapter; the remaining elements of the family will now be considered.

### PHOSPHORUS

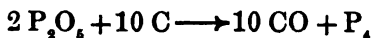
**History.** The element phosphorus was discovered by the alchemist *Brand*, of Hamburg, in 1669, while searching for the philosophers' stone. However, it remained a very rare and costly substance until the demand for it in the manufacture of matches brought about its production on a large scale.

**Occurrence.** Owing to its great chemical activity phosphorus never occurs free in nature. In the form of phosphates it is very abundant and widely distributed. *Phosphorite*,  $\text{Ca}_3(\text{PO}_4)_2$ , is the chief mineral form of calcium phosphate, while *apatite* consists of calcium phosphate together with calcium fluoride or calcium chloride. In the form of *phosphate rock*, these minerals mixed with many impurities are found in large quantities in the United States, especially in Florida and Tennessee in the south and Utah and Idaho in the west, and are mined in enormous quantities (about 3,000,000 tons annually) for use in the manufacture of fertilizers. Calcium phosphate is also a constituent of all fertile soil. It is the chief mineral constituent of the bones of animals, and bone ash is therefore nearly pure calcium phosphate.

**Preparation.** At present phosphorus is usually prepared by heating mineral phosphates or bone ash with coke and sand, in a specially constructed electrical furnace, the main features of which are shown in Fig. 146. At the temperature employed silica is not volatile, while phosphoric anhydride ( $\text{P}_2\text{O}_5$ ) is. The volatile anhydride is displaced:



The carbon present then reduces the oxide of phosphorus:



The charge of phosphate, coke, and sand is fed into the furnace from the hopper *A* by the worm screw *B*, while the liquid calcium silicate is drawn off at *C* as a slag or glass. The vapors of phosphorus escape at *D*, together with the carbon monoxide, and are condensed to a liquid by a suitable water condenser. The liquid is purified by filtration through chamois skin or porous stone, and is finally run into molds immersed in cold water, and hardened into sticks for the market. It is of interest to note that, during the World War, the carbon monoxide generated in the process was utilized in the manufacture of phosgene.

The total production of phosphorus in the United States amounts to about 100 tons monthly. Most of this is prepared at Niagara Falls.

#### White, or yellow, phosphorus.

The phosphorus prepared in this way is called white, or yellow, phosphorus. It is really a colorless, translucent, waxy solid, which melts at  $44^{\circ}$ , boils at  $287^{\circ}$ , and has a density of 1.83 at ordinary temperatures. It is insoluble in water but dissolves readily in many solvents, such as carbon disulfide and turpentine, crystallizing from them in the isometric system. It is an extremely active substance, combining directly with most of the elements, especially with oxygen. When very slightly warmed in the air it takes fire and burns with a sputtering flame, which becomes very brilliant in an atmosphere of oxygen. The product of combustion is the oxide  $P_2O_5$ . The warmth of the fingers is sufficient to bring the substance to its kindling temperature, so that the greatest care is necessary in handling it. It is always preserved and handled under water. It is a violent poison. Measurements of the vapor density of phosphorus show that the vapor has the formula  $P_4$  (p. 400).

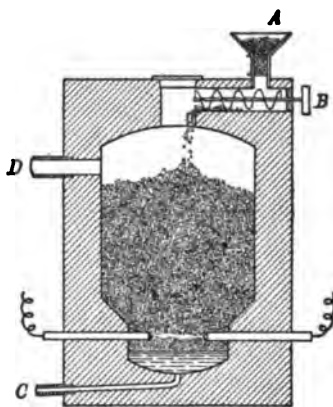


FIG. 146

**The slow combustion of phosphorus.** There are many peculiarities attending the slow combustion of phosphorus. A stick lying half covered with water is slowly oxidized, and ozone, recognizable by its odor and its

action on starch iodide paper, is formed at the same time. Of the total oxygen used up, half goes to oxidize the phosphorus and half to combine with molecular oxygen to form ozone (p. 38). The energy absorbed in the formation of the latter is furnished by the combustion of the phosphorus.

In the slow oxidation of phosphorus, light (which can be seen in a dark room) is given off, though the temperature is far too low for incandescence. This striking phenomenon suggested the name *phosphorus* (light bearer), and although other bodies act in the same way, the phenomenon is called *phosphorescence*. In an atmosphere of pure oxygen there is no phosphorescence. It is only when the partial pressure of the oxygen falls below 320 mm. at 0° that it appears.

**Red phosphorus.** When white phosphorus is heated out of contact with oxygen, it is converted into quite a different body, called *red phosphorus*. This change goes on very slowly at ordinary temperatures, is very marked at about 250°, and at 300° is very rapid. It can be hastened by catalyzers, such as iodine or selenium. If the red phosphorus is vaporized, it gives a vapor which is identical with that from the white form, and on condensation the latter variety is always obtained. This is in accordance with the general rule to the effect that *when a substance capable of existing in several forms is condensed from the gaseous state or crystallized from the liquid state, the least stable variety forms first; and this, on standing, passes into the more stable form.*

Red phosphorus is microcrystalline, is not soluble in any solvent, is not poisonous, and has a smaller heat of combustion than the white form. It does not combine with oxygen at ordinary temperatures and can be handled with entire safety. It has no constant physical properties, varying from scarlet to purple-red in color, and from 2.10 to 2.30 in density. Its heat of combustion is also variable. It is therefore not a homogeneous substance.

**Allotropic forms of phosphorus.** While the white and red phosphorus are the two commercial forms, there appear to be four true allotropic forms of the element: (1) ordinary isometric white phosphorus; (2) a second white form obtained by cooling white phosphorus below - 80°; (3) violet phosphorus, obtained by heating white or red phosphorus several days

above 450°; (4) black phosphorus, obtained by heating the white form to 200° under very high pressure (12,500 atmospheres). Red phosphorus is an incomplete conversion of white phosphorus into the violet form.

**Uses of phosphorus.** Small amounts of the element are used as a rat poison and for minor purposes in chemical laboratories. It is also used in making pure phosphoric acid. The great consumption, however, is in the manufacture of matches.

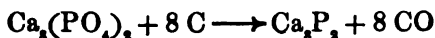
During the World War large amounts were used in generating smoke clouds. Phosphorus burns readily, forming a dense white smoke (oxide of phosphorus) which served admirably for concealing troops and ships.

**Matches.** Friction matches containing phosphorus first came into use in 1827, and at present two general varieties are in common use. The more common variety is made by dipping the match stick first into some inflammable substance, such as melted paraffin, and afterwards into a paste consisting of (1) phosphorus sesquisulfide,  $P_4S_6$ ; (2) some oxidizing substance, such as manganese dioxide, red lead, or potassium chlorate; and (3) a binding material, such as glue or dextrin. On friction the phosphorus is ignited, the combustion being supported by the oxidizing agent and communicated to the wood by the burning paraffin. In sulfur matches the paraffin is replaced by sulfur.

In the Swedish, or safety, match, red phosphorus, an oxidizing agent, and some gritty material, such as powdered glass, are mixed with glue and placed on the side of the box. The match tip is provided with an oxidizing agent and an easily combustible substance, usually antimony sulfide. The match cannot be ignited easily by friction except on the prepared surface.

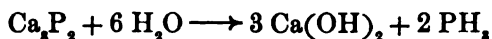
Constant working with white phosphorus frequently results in dreadful diseases of the bones of the face, while many disastrous fires are caused by accidental ignition of matches containing it. On both accounts the manufacture and use of such matches is prohibited by law in many countries. The Congress of the United States in 1913 accomplished the same end by imposing a prohibitive tax upon white phosphorus matches. Both the export and import of such matches is also prohibited.

**Phosphides.** Phosphorus combines directly with the great majority of the elements forming *phosphides*. Many of the metallic phosphides can be obtained by reducing the corresponding phosphate with carbon:

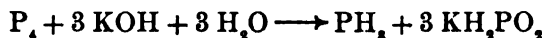


Some iron ores, especially limonite, contain iron phosphate, and the production of iron phosphide during the reduction of the ore is a source of trouble in steel making, since it is apt to remain dissolved in the metal.

**Phosphides of hydrogen; the phosphines.** Phosphorus forms three compounds with hydrogen, known as the *phosphines*. They are  $\text{PH}_3$ , a gas;  $\text{P}_2\text{H}_4$ , a colorless liquid; and  $\text{P}_{12}\text{H}_6$ , a yellow, flocculent solid. Of these, gaseous phosphine is the best known and is the one referred to when the term *phosphine* is used. Like the hydrogen compounds of most of the nonmetals, it can be prepared by decomposing a metallic phosphide by water or an acid:



It is more easily prepared from familiar reagents by boiling white phosphorus with a concentrated solution of a strong base. The reaction is rather complicated, the equation being



**Preparation of phosphine.** The compound may be conveniently prepared by the use of the apparatus illustrated in Fig. 147. A 200-cc. flask *A* is half

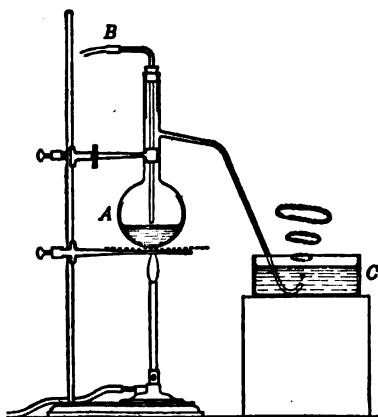


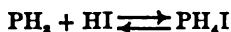
FIG. 147

filled with a concentrated solution of potassium hydroxide, a few small pieces of phosphorus are dropped in, and the air in the flask is displaced by a current of coal gas admitted through *B*. When the contents of the flask are heated, phosphine is formed, and, passing through the delivery tube, is liberated just under the surface of the water in *C*. As each bubble makes its escape into the air it takes fire spontaneously and forms a ring of white smoke, consisting of phosphorus pentoxide ( $\text{P}_2\text{O}_5$ ).

The gas has a disagreeable odor and is very poisonous. It boils at  $-86.2^\circ$ . It burns readily but is not spontaneously inflammable. In its preparation some of the liquid phosphine

is formed, which, being spontaneously inflammable, ignites the gas. The latter may be freed from the liquid by bubbling it through alcohol, in which the liquid phosphine is soluble, or by conducting it through a freezing mixture which condenses the higher-boiling product to the liquid state.

In formula, gaseous phosphine resembles ammonia, but in the presence of water it has no basic properties. When dry it will combine with the hydrides of the halogens, forming compounds which in formula resemble ammonium salts, and which on this account are called *phosphonium salts*. The best known of these is the iodide, which sublimes in colorless, glittering crystals:



The action is reversible, and in the air the solid rapidly dissociates into its components. The chloride and bromide are formed only under increased pressure. It will be shown in a later chapter that the ammonium halides dissociate in the same way when heated, but that the temperature at which dissociation becomes perceptible is much higher. Liquid phosphine ( $\text{P}_2\text{H}_4$ ) is colorless and strongly refracts light. It boils at  $57^\circ$  and has about the same density as water. It is analogous in formula to hydrazine ( $\text{N}_2\text{H}_4$ ), and the two compounds have many analogous derivatives, although phosphine has no basic properties.

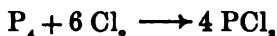
**Halogen compounds.** Phosphorus combines with the several halogens directly and with the greatest ease, forming two series of compounds. In the one it is trivalent and in the other, with the exception of the iodide, pentavalent. A table of these compounds will indicate their characteristics:

THE HALOGEN COMPOUNDS OF PHOSPHORUS

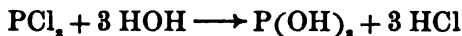
	MELTING POINT	BOILING POINT	HEAT OF FORMATION
Trifluoride . . . . . $\text{PF}_3$	— 160.0	— 95	108,000 cal.
Pentafluoride . . . . . $\text{PF}_5$	— 83.0	— 75	
Trichloride . . . . . $\text{PCl}_3$	< — 115.0	76	76,000 cal.
Pentachloride . . . . . $\text{PCl}_5$	148.0	140	107,000 cal.
Tribromide . . . . . $\text{PBr}_3$	41.5	175	44,800 cal.
Pentabromide . . . . . $\text{PBr}_5$	decomp.	decomp.	63,000 cal.
Tetra-iodide . . . . . $\text{P}_2\text{I}_4$	110.0	decomp.	19,800 cal.
Tri-iodide . . . . . $\text{PI}_3$	60.0	decomp.	10,900 cal.

Only the compounds with chlorine will be described, as they are the best known and have important uses. The others are made by analogous methods and have similar chemical characteristics.

**Phosphorus trichloride ( $\text{PCl}_3$ ).** This liquid is obtained by passing a current of dry chlorine over white phosphorus:



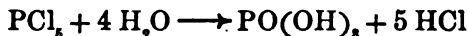
It is a colorless liquid, of density 1.6, which fumes strongly in the air, owing to the action of moisture upon it:



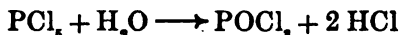
**Phosphorus pentachloride ( $\text{PCl}_5$ ).** The solid, pale-yellow pentachloride is obtained by passing chlorine into the trichloride, the reaction being attended by the evolution of considerable heat:



When the solid pentachloride is heated to a moderately high temperature, this action is reversed and dissociation occurs, just as in the case of ammonium chloride. The melting point can be determined only when the substance is confined in a sealed tube, which prevents the vapors from escaping. Like the trichloride, this substance acts upon water and other hydroxyl compounds. With excess of water the reaction is

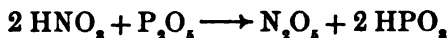


When insufficient water is present, a liquid oxychloride is formed, called *phosphoryl chloride*:



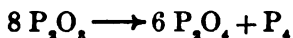
**Oxides of phosphorus.** Three oxides of phosphorus are known, namely,  $\text{P}_2\text{O}_3$ ,  $\text{P}_2\text{O}_4$ , and  $\text{P}_4\text{O}_6$ . Vapor-density determinations show that the latter has the double formula  $\text{P}_4\text{O}_6$ , but it is more convenient to use the simpler formula  $\text{P}_2\text{O}_3$ , especially since the molecular weight of the other oxides is not known, and the compound is usually called the trioxide. Moreover, we have no knowledge as to the molecular weight of any of these compounds in the solid state.

**Phosphorus pentoxide ( $P_2O_5$ ).** The pentoxide is obtained as a snowlike solid by the complete combustion of phosphorus. It volatilizes only at a white heat. Its heat of formation is very great, namely, 369,900 cal., and accordingly it is very stable and has almost no oxidizing properties. Its most remarkable characteristic is its activity toward water, with which it combines with great energy. On this account it is the most effective drying agent known, very considerably surpassing calcium chloride and sulfuric acid. It will also abstract the elements of water from many hydroxyl compounds. For example, it converts many acids into anhydrides, as shown in the equation



The use of the oxide during the World War for the formation of smoke clouds has already been noted (p. 463).

**Phosphorus trioxide ( $P_2O_3$  or  $P_4O_6$ ).** This oxide is formed by burning phosphorus under conditions which do not provide enough oxygen for complete combustion. It often occurs as an impurity in the pentoxide. This also is a snowlike solid, which melts at  $22.5^\circ$  and boils at  $173.1^\circ$ , so it can be separated from the pentoxide by distillation. The tetroxide  $P_4O_{10}$ , a colorless crystalline solid, is formed by heating the trioxide:



**The acids of phosphorus.** The pentoxide and trioxide are both typical acid anhydrides. They combine with water directly and each gives rise to a number of acids which differ from each other not in the valence of the phosphorus but in the ratio between the oxide and the water. Their formulas and relations are shown in the following table:

PHOSPHORIC ACIDS		PHOSPHOROUS ACIDS	
Ortho-	$\text{P}_2\text{O}_5 + 3 \text{H}_2\text{O} \longrightarrow 2 \text{H}_3\text{PO}_4$	Ortho-	$\text{P}_2\text{O}_3 + 3 \text{H}_2\text{O} \longrightarrow 2 \text{H}_3\text{PO}_3$
Pyro-	$\text{P}_2\text{O}_5 + 2 \text{H}_2\text{O} \longrightarrow \text{H}_4\text{P}_2\text{O}_7$	Pyro-	$\text{P}_2\text{O}_3 + 2 \text{H}_2\text{O} \longrightarrow \text{H}_4\text{P}_2\text{O}_6$
Meta-	$\text{P}_2\text{O}_5 + \text{H}_2\text{O} \longrightarrow 2 \text{HPO}_3$	Meta-	$\text{P}_2\text{O}_3 + \text{H}_2\text{O} \longrightarrow 2 \text{HPO}_2$

**The phosphoric acids.** Since all three of the phosphoric acids are derived from the stable pentoxide, it is not surprising that they share its stability as regards reduction.

1. *Orthophosphoric acid* ( $H_3PO_4$ ). This acid, representing the greatest degree of hydration of the stable oxide, is the form into which all other acids of phosphorus tend to pass when in solution. Pure hydrogen phosphate is prepared by burning white phosphorus in air and completing the oxidation with nitric acid. The compound forms colorless crystals, which melt at  $40^\circ$ . A commercial grade of acid is prepared by treating calcium phosphate with concentrated sulfuric acid and filtering off the insoluble calcium sulfate:

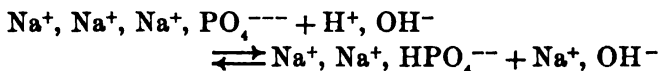
$$Ca_3(PO_4)_2 + 8 H_2SO_4 \longrightarrow 3 CaSO_4 + 2 H_3PO_4$$

In solution hydrogen phosphate is an acid of medium strength and is tribasic. It is therefore capable of forming three series of salts, according as one, two, or three hydrogen atoms are replaced by metals. The composition and method of naming such salts are illustrated in the following table, which gives the formulas and the different names of the three sodium salts:

FORMULA	NAME
$Na_3PO_4$ . . .	Trisodium phosphate; normal, or tertiary, sodium phosphate
$Na_2HPO_4$ . . .	Disodium phosphate; secondary sodium phosphate
$NaH_2PO_4$ . . .	Monosodium phosphate; primary sodium phosphate

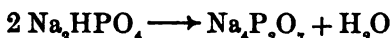
The heavy metals, such as silver or mercury, form only the normal, or tertiary, phosphates. Mixed salts are also known, the most familiar ones being microcosmic salt ( $NaNH_4HPO_4 \cdot 4 H_2O$ ) and magnesium ammonium phosphate ( $MgNH_4PO_4$ ).

The normal salts of the alkali metals, sodium and potassium, are very strongly hydrolyzed in solution:



Even the secondary salt  $Na_2HPO_4$ , which is the common sodium phosphate, has a decidedly basic reaction in solution.

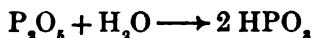
2. *Pyrophosphoric acid* ( $H_4P_2O_7$ ). This acid can be obtained by heating the orthophosphoric acid to  $218^\circ$ . It forms a colorless glassy mass which melts at about  $61^\circ$ . Its sodium salt is prepared by heating ordinary sodium phosphate, and from this salt others are readily obtained:



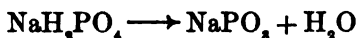
3. *Metaphosphoric acid* ( $HPO_3$ ). Metaphosphoric acid is obtained by strongly heating either the ortho or the pyro acid:



It is the first product formed when the pentoxide acts upon water:

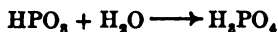


It melts at a high temperature and, on cooling, forms a glass called glacial phosphoric acid. At very high temperatures it is volatile. Its sodium and potassium salts can be obtained by heating the corresponding primary orthophosphate:

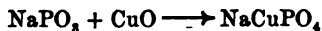


While its simplest formula is  $HPO_3$ , both the acid and its salts exist in a variety of polymeric forms, the acids having the general formula  $(HPO_3)_n$ , in which  $n$  is an integer.

**Use of metaphosphates as fluxes.** When metaphosphoric acid is dissolved in water, it slowly combines with it, forming orthophosphoric acid:



In a similar way, when sodium metaphosphate is heated with metallic oxides, it forms mixed salts of orthophosphoric acid:



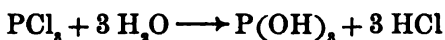
The salts so formed remain dissolved in the excess of metaphosphate and, on cooling, harden to a glass. This frequently acquires a color which is characteristic of the oxide so dissolved, and suggests a method of testing for the presence of certain metals in materials of unknown composition.

A bead of the metaphosphate is first formed by fusing a crystal of microcosmic salt on a loop of wire in a Bunsen flame:

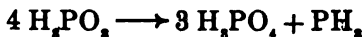


This bead is then dipped into the powdered material to be examined, and reheated. The color, both while hot and when cold, shows the presence of certain metals, such as iron, copper, cobalt, and chromium. It will be seen that the principle is the same as in the case of the borax bead (p. 502).

**The phosphorous acids.** The only one of the phosphorous acids at all well known is orthophosphorous acid,  $\text{H}_3\text{PO}_3$ , commonly called merely phosphorous acid. It is best prepared by treating phosphorus trichloride with water:



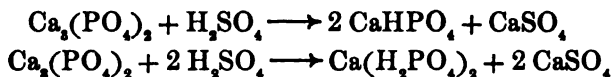
It can be obtained from solution in large, transparent crystals melting at  $71^\circ$ . Although it contains three atoms of hydrogen in the molecule, it is a *dibasic* acid, only two of the hydrogen atoms being replaceable by metals. On this account its formula is sometimes written  $\text{H}_2 \cdot \text{HPO}_3$ . Like the trioxide from which it is derived, it takes up oxygen very readily and is a strong reducing agent. When heated by itself it undergoes an interesting reaction, in which one portion is oxidized to phosphoric acid, while another is reduced to phosphine:



**Hypophosphorous acid ( $\text{H}_3\text{PO}_2$ ).** There are a number of acids of phosphorus which are not derived from any known oxide, the most important one being hypophosphorous acid. When white phosphorus is boiled with concentrated potassium hydroxide (see preparation of phosphine), the salt  $\text{KH}_2\text{PO}_2$  is obtained, and from this the free acid, as well as other salts, can be prepared. The acid crystallizes in beautiful transparent crystals, which melt at  $17.4^\circ$ . Although it contains three atoms of hydrogen in the molecule, it is a *monobasic* acid, the formula being sometimes written  $\text{H} \cdot \text{H}_2\text{PO}_2$ . Both the acid and all its salts are soluble in water and are strong reducing agents. The hypophosphites find frequent applications in medicine.

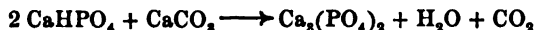
**Fertilizers.** Phosphorus appears to be essential to both animal and vegetable organisms and must, as a consequence, be present in every fertile soil. Since crops are constantly removed

from cultivated land, and since phosphorus compounds are never very abundant in it, the soil is gradually exhausted of this element, the supply of which must be renewed in some way. Animal manures are of the greatest value not only for phosphorus but also for nitrogen compounds, but the supply is never sufficient. The large deposits of rock phosphate referred to above are the only source from which an adequate supply can be derived. The pulverized rock is sometimes applied directly, but usually it is first treated with sulfuric acid, when one or both of the reactions expressed in the following equations take place:



This treatment appears greatly to increase the value of the rock as a fertilizer. Doubtless this is partly due to the increase in the solubility of the phosphorus compounds, for the normal calcium phosphate is practically insoluble in water, while the primary salt  $\text{Ca}(\text{H}_2\text{PO}_4)_2$  is freely soluble, and the secondary salt  $\text{CaHPO}_4$ , though insoluble in water, is soluble in weak organic acids, such as are present about the roots of growing plants.

When, however, these compounds are spread upon the soil, which usually contains oxides or carbonates of basic character, the normal salt must be formed once more. This reaction, whether taking place in the soil or in the stored fertilizer, is called *reversion*. The reaction with limestone will illustrate this reversion:

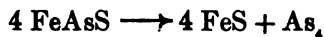


In reversion the normal salt is precipitated in a very fine state of division, and is much better distributed throughout the soil than could be accomplished by mechanical means, which may partly explain the value of acid treatment. It is also true that calcium sulfate is beneficial to some soils, since sulfur must be present in small amounts. Care must be exercised to avoid excess of sulfuric acid in the treatment of the rock, since this injures many soils. It is clear that a given soil may cease to be productive through many different causes, and there are many cases in which the application of a phosphate fertilizer would be of no value whatever.

## ARSENIC

**History and occurrence.** Compounds of arsenic have been known from the earliest times. The highly colored sulfides, *realgar* ( $\text{As}_2\text{S}_2$ ) and *orpiment* ( $\text{As}_2\text{S}_3$ ), are found in nature, and have been used as pigments since the time of Aristotle. *Arsenopyrite* ( $\text{FeAsS}$ ), known as *mispickel*, is an abundant mineral, and the corresponding *cobaltite* ( $\text{CoAsS}$ ) is not rare. The element is occasionally found in the free form, and also as the oxide  $\text{As}_2\text{O}_3$ , called *arsenolite*. It is also very widely distributed in traces throughout the sulfide ores of many metals, and these metals, as well as products prepared from the sulfur derived from the ores, are apt to be contaminated with arsenic. Practically all the arsenic used in the United States is obtained in the form of the trioxide  $\text{As}_2\text{O}_3$ , as a by-product in the smelting of copper ores.

**Preparation and properties.** The element is prepared by subliming the natural product or by heating mispickel:



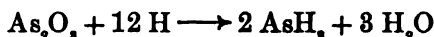
It is prepared in pure form by reducing the oxide with carbon, the arsenic being easily volatile and condensing again on a cold surface. Like phosphorus, it occurs in several distinct forms. The most important of these is the so-called gray or metallic arsenic, which, when the vapor of arsenic is slowly cooled, is obtained as a gray crystalline mass somewhat resembling coke in appearance. When heated its vapor pressure increases rapidly, reaching 760 mm. much below its melting point; hence it sublimates very easily. It is very brittle and has a density of 5.73. All forms give the same yellowish vapor, the density of which corresponds to the formula  $\text{As}_4$ . When heated in air, arsenic forms the oxide  $\text{As}_2\text{O}_3$ . It combines with chlorine, forming the trichloride  $\text{AsCl}_3$ .

The element readily alloys with some of the metals, and finds its chief use as an alloy with lead which is used for making shot. The alloy is harder than pure lead and the shot made from it is more nearly spherical.

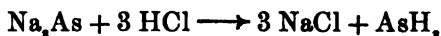
**Arsenides.** Arsenic combines directly with most of the elements, forming *arsenides*. With the nonmetallic elements these compounds are for the most part decomposed by water. The metallic arsenides are frequently formed in the reduction of metals whose ores carry some arsenic. They are usually stable compounds, are strongly metallic in appearance, and are soluble in many melted metals. Many of them may be obtained by heating the metal with arsenic or by reducing an arsenate:



**Arsenic hydride (arsine) ( $\text{AsH}_3$ ).** Arsenic forms only one hydride, the colorless gas *arsine* ( $\text{AsH}_3$ ). It is formed when hydrogen is liberated in contact with an arsenic compound:



It can be prepared free from hydrogen by the action of hydrochloric acid upon sodium arsenide:



It is a gas which liquefies at  $-55^\circ$  and solidifies at  $-119^\circ$ . It has an odor like that of garlic and is *extremely poisonous*. It is very unstable and burns in air with a bluish-white flame forming arsenic trioxide ( $\text{As}_2\text{O}_3$ ) and water. It is decomposed into its elements by a very moderate heat. This is easily demonstrated by conducting the gas through a tube heated at one point, the arsenic depositing as a black mirror a little beyond the hot region. Owing to the form in which it is deposited, a mere trace is easily seen. Because of this ready decomposition arsine is a strong reducing agent.

**Marsh's test for arsenic.** The properties of arsine make possible the use of a very delicate method for

detecting its presence, known as Marsh's test. Hydrogen is generated in a flask *A* (Fig. 148) by the action of hydrochloric acid upon zinc, the escaping gases being dried by passing through a calcium chloride tube *B*.

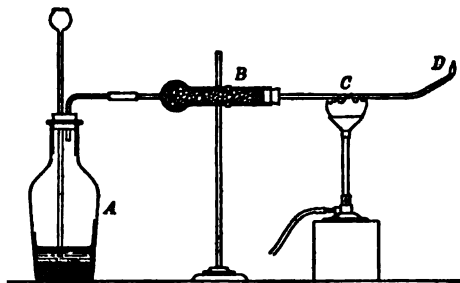


FIG. 148

Heat is applied at *C* for some time, and, if no mirror forms, the reagents are free from arsenic. The material to be tested is brought into solution by the necessary preliminary treatment and is introduced through the funnel tube, the presence of arsenic being indicated by the speedy formation of a mirror. Instead of heating the tube a cold porcelain dish may be held in the flame at *D*, the arsenic being deposited upon it as a dark spot. The mirror is a very brilliant black, is brownish at the edges, is very easily volatilized when heated, dissolves readily in a solution of sodium hypochlorite, and turns yellow on conducting a current of hydrogen sulfide through the tube. All these characteristics distinguish the arsenic mirror from a similar one produced by the element antimony. Under favorable conditions the presence of a quantity of arsenic no greater than 0.1 mg. can be detected. Indeed, it is difficult to secure zinc and acid for generating hydrogen which will not give a test for arsenic.

**Halogen compounds.** The well-known halogen compounds of arsenic are derived from the trivalent element, their chief physical constants being given in the table. The pentafluoride  $\text{AsF}_5$  and possibly the pentachloride  $\text{AsCl}_5$  are also known.

HALOGEN COMPOUNDS OF ARSENIC

	DENSITY	MELTING POINT	BOILING POINT	COLOR
Trifluoride . . $\text{AsF}_3$	2.7 liquid	- 8.3	63.3	Colorless
Trichloride . . $\text{AsCl}_3$	2.2 liquid	- 18.0	130.2	Colorless
Tribromide . . $\text{AsBr}_3$	3.7 solid	31.0	221.0	Colorless
Tri-iodide . . $\text{AsI}_3$	4.4 solid	146.0	400.0	Red

These compounds are decomposed by water, but not so readily as in the case of the corresponding phosphorus compounds. This is seen from the fact that arsenious oxide ( $\text{As}_2\text{O}_3$ ) dissolves in concentrated hydrochloric acid, though it is but sparingly soluble in water. When the solution is boiled, some of the arsenic passes off with the vapor; this does not happen when a solution of the oxide in water is boiled. Arsenic chloride is therefore present in the solution:  $\text{As}_2\text{O}_3 + 6 \text{HCl} \rightleftharpoons 2 \text{AsCl}_3 + 3 \text{H}_2\text{O}$

**Oxides of arsenic.** There are two oxides of arsenic: the trioxide  $\text{As}_2\text{O}_3$ , or  $\text{As}_4\text{O}_6$ , and the pentoxide  $\text{As}_2\text{O}_5$ . These are both acid anhydrides.

**Arsenic trioxide (white arsenic)** ( $\text{As}_2\text{O}_3$  or  $\text{As}_4\text{O}_6$ ). As a matter of convenience the formula of this oxide is usually written  $\text{As}_2\text{O}_3$ , although the vapor-density measurements show that it should be  $\text{As}_4\text{O}_6$ . The oxide is found in nature in several forms, and it is obtained as a by-product in the smelting of copper ores. In this process the arsenic is converted into oxide, which condenses in the flues as a fine dust from which the pure oxide may be obtained by sublimation, as it is readily volatile. When sublimed with slow cooling, the product is a transparent amorphous glass, which gradually becomes opaque, like porcelain, owing to crystallization. When condensed rapidly, it forms a crystalline powder of very characteristic appearance.

The ready formation of this crystalline deposit is turned to practical account in testing for the presence of the oxide. The material to be tested is placed in a small test tube of hard glass and is heated in a Bunsen flame. If arsenic oxide is present, it will deposit in characteristic white crystals upon the colder walls of the tube, as shown in Fig. 149.

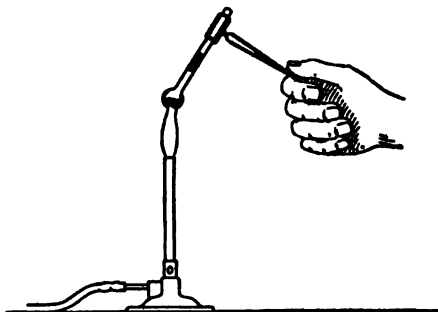
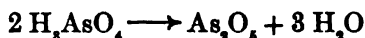


FIG. 149

The oxide is only slightly soluble in water. It has a weak, sweetish taste and is *very poisonous*, but the system can become accustomed to it by gradually increasing the dose. Some mountaineers believe that it increases their endurance in mountain climbing, and they gradually become accustomed to daily portions four times as large as a fatal dose for an ordinary person.

**Uses.** Arsenic trioxide has extensive uses. It is the compound from which all other arsenic compounds are prepared. Its greatest use is in the preparation of insecticides for spraying trees and destroying insects on stock. It is also used in making glass, to remove objectionable air bubbles. On a smaller scale it is used in medicine and as a preservative in taxidermy.

**Arsenic pentoxide ( $\text{As}_2\text{O}_5$ ).** This oxide, a white amorphous solid, cannot be obtained by the direct combustion of arsenic or of the trioxide, but is made by heating arsenic acid:



It is not very stable toward heat, and at a high temperature dissociates into the trioxide and oxygen; consequently its molecular weight is unknown. It is a moderately strong oxidizing agent.

**Acids of arsenic.** Arsenic forms two series of oxygen acids derived from the two oxides analogous to those of phosphorus. The names and formulas of these are as follows:

ARSENIOUS ACIDS	ARSENIC ACIDS
Orthoarsenious acid . . . . $\text{H}_2\text{AsO}_3$	Orthoarsenic acid . . . . $\text{H}_2\text{AsO}_4$
Pyroarsenious acid . . . . $\text{H}_4\text{As}_2\text{O}_5$	Pyroarsenic acid . . . . $\text{H}_4\text{As}_2\text{O}_7$
Metarsenious acid . . . . $\text{HAsO}_2$	Metarsenic acid . . . . $\text{HAsO}_3$

**The arsenious acids.** When dissolved in water, arsenic trioxide gives rise to a number of different acids, none of which have been obtained in pure condition and all of which are very weak. By suitable means the salts of these acids can be obtained, those of sodium and potassium being derived from the metarsenious acid  $\text{HAsO}_2$ , while those of most of the other metals are derived from the ortho acid  $\text{H}_2\text{AsO}_3$ . Thus the potassium salt is  $\text{KAsO}_2$ , while the silver salt is  $\text{Ag}_3\text{AsO}_3$ . Salts of the pyro acid  $\text{H}_4\text{As}_2\text{O}_5$  are also known. The copper salts are of importance. *Scheele's green* ( $\text{CuHAsO}_3$ ) is used as a pigment. *Paris green* is used as a poison for insects. It is a double salt of the formula  $\text{Cu}_3(\text{AsO}_3)_2 \cdot \text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2$ . Freshly precipitated ferric hydroxide forms an insoluble product with arsenical compounds which is not poisonous and is the best antidote for arsenic poisoning.

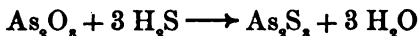
**The arsenic acids.** When arsenic trioxide is boiled with nitric acid and the solution is evaporated to a sirup, crystals of orthoarsenic acid are obtained, which have the formula  $2 \text{H}_2\text{AsO}_4 \cdot \text{H}_2\text{O}$ .

When these crystals are heated from  $140^{\circ}$  to  $180^{\circ}$ , they lose water and form the pyro acid  $H_4As_2O_7$ . When they are heated to  $200^{\circ}$ , the meta acid  $HAsO_3$  is formed. All these acids, when dissolved in water, are again converted into the ortho acid. Salts of this latter acid are not infrequently found in nature, and many have been prepared in the laboratory. *Lead arsenate* is largely used as an insecticide for spraying fruit trees. The commercial product is usually a mixture of  $Pb_3(AsO_4)_2$  and  $PbHAsO_4$ . The reddish-brown silver salt  $Ag_3AsO_4$  and the magnesium ammonium salt  $MgNH_4AsO_4$  are of importance in analytical chemistry. All these salts are quite similar to the corresponding phosphates. Unlike phosphoric acid, arsenic acid is an oxidizing agent, as might be anticipated from the instability of its anhydride.

**Sulfides of arsenic.** There are three well-known sulfides of arsenic, namely,  $As_2S_3$ ,  $As_2S_5$ , and  $As_4S_6$ .

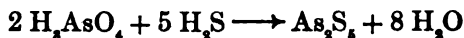
**Arsenic disulfide (realgar) ( $As_2S_3$ ).** Realgar is found in nature as very beautiful red crystals, and is artificially prepared by heating arsenic with sulfur in the proper proportions. It was formerly much used as a pigment.

**Arsenic trisulfide (orpiment) ( $As_2S_3$ ).** This substance is found in nature in yellow crystals, and is artificially prepared by heating a mixture of arsenic and sulfur. In the laboratory it results as an amorphous yellow precipitate when hydrogen sulfide is conducted into an acidulated solution of an arsenious compound:

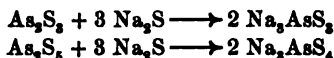


If the solution is neutral or basic, no precipitate forms, although the solution turns yellow. This will be explained in the chapter on Colloids.

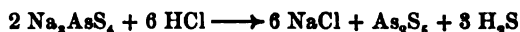
**Arsenic pentasulfide ( $As_4S_6$ ).** The pentasulfide is slowly precipitated as a curdy yellow precipitate when hydrogen sulfide is conducted into a solution of arsenic acid containing hydrochloric acid:



**Thio salts of arsenic.** When either the trisulfide or the pentasulfide is treated with a solution of a *soluble sulfide*, such as sodium sulfide ( $\text{Na}_2\text{S}$ ) or ammonium sulfide  $(\text{NH}_4)_2\text{S}$ , it is dissolved, and when the solution is evaporated, well-crystallized *thio salts* are obtained:



These salts may be regarded as derived from the corresponding oxygen salts by the replacement of oxygen with sulfur. Thio salts corresponding to both the pyro and the meta acids are also known. All these salts are easier to obtain in well-crystallized form than the oxygen salts. On treatment with acids they are decomposed, with the formation of sulfides:



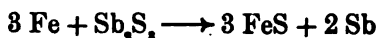
These reactions make it possible to separate the sulfides of arsenic from those of other elements which are insoluble in the sulfides of sodium or ammonium.

### ANTIMONY

**Historical.** Compounds of antimony, as well as the element itself, have been known from the earliest times. The Chaldeans appear to have made ornamental vessels of the metal. The Chinese employed preparations of antimony as drugs. The sulfide  $\text{Sb}_2\text{S}_3$ , known as *stibnite*, was called *stibium* by Pliny, the name *antimonium* first appearing in the works of the alchemist Geber. In the fifteenth century, compounds of antimony were widely used as medicines.

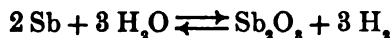
**Occurrence and metallurgy.** The chief ore of antimony is stibnite. This is rather widely distributed in different countries, but the supply comes principally from China, Japan, and France. The United States produces a small amount only.

A number of processes are used in obtaining the metal from its ore. In China, which country produces by far the largest amount, the ore is roasted to produce the oxide,  $\text{Sb}_2\text{O}_3$ , which is then reduced by carbon. Rich ores are generally treated by heating with iron, which combines with the sulfur, the iron sulfide produced acting as a flux for the antimony:



**Properties.** Like phosphorus and arsenic, antimony exists in several distinct forms, the familiar one being the ordinary gray form. The latter is a silvery, shining metal, very brittle, and forms crystals which, like those of gray arsenic, belong to the hexagonal system. Its density is 6.7, its melting point  $630^{\circ}$ , and its boiling point  $1440^{\circ}$ . Its vapor density indicates that the vapor is a mixture of molecules of the formulas  $\text{Sb}_2$  and  $\text{Sb}_4$ .

**Chemical conduct.** In its compounds antimony may be either pentavalent, quadrivalent, or trivalent. In the compounds in which it is trivalent it plays the part of a metal; as a pentavalent element it is, like arsenic, a nonmetal. It stands midway between arsenic, which is strictly acid-forming, and bismuth, which is base-forming. Antimony is not attacked by dilute acids, being below hydrogen in the electrochemical series. Concentrated sulfuric acid converts it into the sulfate,  $\text{Sb}_2(\text{SO}_4)_3$ , with liberation of sulfur dioxide, and nitric acid oxidizes it to the pentavalent condition, forming the solid  $\text{H}_3\text{SbO}_4$ . At ordinary temperatures it is very little acted upon by oxygen, but as a powder it is readily combustible. It acts upon steam, liberating hydrogen:

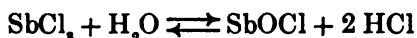


**Antimony hydride (stibine) ( $\text{SbH}_3$ ).** Antimony forms only one hydride ( $\text{SbH}_3$ ), corresponding to phosphine and arsine. It is obtained by methods analogous to those employed with arsine, namely, by the action of acids on metallic antimonides, such as those of zinc or magnesium, and by the action of nascent hydrogen on antimony compounds. It is a gas which liquefies at  $-18^{\circ}$  and solidifies at  $-91.5^{\circ}$ , and it has an odor suggesting that of hydrogen sulfide. In chemical conduct it closely resembles arsine but is more easily decomposed by heat (at  $150^{\circ}$  to  $200^{\circ}$ ), and the mirror formed in a cold tube is readily distinguished from that of arsenic, as already described (p. 474).

**Halogen compounds of antimony.** Antimony forms an almost complete double series of halogen compounds, the pentabromide alone being unknown. They can be prepared by direct union of

the elements, and in some cases by the action of the halogen acid upon antimony or its oxides.

Most of these compounds are partially decomposed by water, the reaction coming to an equilibrium before it is entirely completed. With the chloride the chief product of the hydrolysis is the oxychloride  $\text{SbOCl}$ :



The following table gives the chief characteristics of these compounds:

THE HALOGEN COMPOUNDS OF ANTIMONY

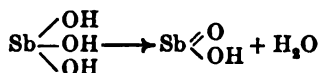
	MELTING POINT	BOILING POINT	COLOR
Trifluoride . . . . . $\text{SbF}_3$	292.0		Colorless crystals
Pentafluoride . . . . . $\text{SbF}_5$	7.0	149.0	Oily liquid
Trichloride . . . . . $\text{SbCl}_3$	73.2	223.0	Colorless crystals
Pentachloride . . . . . $\text{SbCl}_5$	- 6.0	140.0 decomp.	Colorless liquid
Tribromide . . . . . $\text{SbBr}_3$	90.0	275.4	Colorless crystals
Tri-iodide . . . . . $\text{SbI}_3$	167.0	401.0	Ruby-red crystals
Pentiodide . . . . . $\text{SbI}_5$	78.0	decomp.	Dark-brown solid

**Oxides of antimony.** Antimony forms three oxides:  $\text{Sb}_2\text{O}_3$ , a white solid;  $\text{Sb}_2\text{O}_4$ , a white powder;  $\text{Sb}_2\text{O}_5$ , a yellow powder.

**Antimony trioxide ( $\text{Sb}_2\text{O}_3$  or  $\text{Sb}_4\text{O}_6$ ).** This oxide is sometimes found in nature and is prepared by burning metallic antimony in air and subliming the product. It crystallizes in minute cubes, and its vapor density shows it to have the double formula  $\text{Sb}_4\text{O}_6$ , as in the case of the corresponding oxide of arsenic. It is white when cold but yellow when heated. It is insoluble in water and in most dilute acids but is soluble in the halogen acids.

**Amphoteric hydroxides.** The corresponding hydroxide  $\text{Sb}(\text{OH})_3$  is a white, amorphous precipitate which loses water in several stages, finally passing into the oxide. Suspended in water, it dissolves both in acids and in bases, showing that it can act either as a weak base or as a weak acid. *A hydroxide possessing such properties is said to be amphoteric.*

In the *presence of strong bases* it acts as an acid and forms salts analogous to metarsenites derived from the acid  $\text{HSbO}_3$ . An example is the sodium salt  $\text{NaSbO}_3 \cdot 3 \text{H}_2\text{O}$ . The structure of this acid can be inferred from the relation which it sustains to the hydroxide:



When this partially dehydrated hydroxide is *acted upon by an acid*, it acts as a base and forms a salt of the general type  $\text{Sb} \begin{array}{c} \text{O} \\ \diagdown \text{Cl} \end{array}$  or  $\text{Sb} \begin{array}{c} \text{O} \\ \diagdown \text{NO}_3 \end{array}$ . In these salts the group  $\text{SbO}$  plays the part of a univalent radical to which the name *antimonyl* has been given, the two whose formulas have just been mentioned being antimonyl chloride and nitrate respectively. A number of salts are also known in which the antimony hydroxide acts as a tri-acid base. Among these are the halogen salts and the sulfate  $\text{Sb}_2(\text{SO}_4)_3$ .

**Antimony pentoxide ( $\text{Sb}_2\text{O}_5$ ).** The pentoxide is an amorphous yellow powder formed by carefully heating the nitrate. Above  $400^\circ$  it decomposes into the tetroxide  $\text{Sb}_2\text{O}_4$  and oxygen. From it are derived three acids similar to those of phosphorus and arsenic:

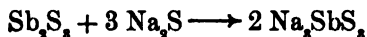
Orthoantimonic acid ( $\text{H}_5\text{SbO}_4$ ), an insoluble white powder  
Pyroantimonic acid ( $\text{H}_4\text{Sb}_2\text{O}_7$ ), an insoluble white powder  
Metantimonic acid ( $\text{HSbO}_3$ ), an insoluble white powder

Many salts of these acids are known, the sodium salts being remarkable for the fact that they are but sparingly soluble, which is very unusual for sodium salts. Both the salts and the acids have oxidizing properties, as would be expected from the ease with which the oxide decomposes.

**Sulfides of antimony.** Three sulfides of antimony are known, having the formulas  $\text{Sb}_2\text{S}_3$ ,  $\text{Sb}_4\text{S}_6$ ,  $\text{Sb}_2\text{S}_5$ . The second is of little importance.

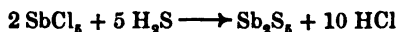
**Antimony trisulfide (stibnite) ( $\text{Sb}_2\text{S}_3$ ).** In nature this substance is found in brilliant black prisms. By conducting hydrogen sulfide into a solution of an antimony salt the same compound is formed as an orange-red precipitate. It is more readily soluble

in concentrated acid than the corresponding arsenic trisulfide. Like the latter, it dissolves in solutions of alkaline sulfides to form a thio salt:



These thio salts are decomposed by acids reprecipitating the sulfide. Antimony trisulfide is easily combustible and is used in the manufacture of matches. It is also used in the vulcanizing and coloring of rubber and as a pigment.

**Antimony pentasulfide ( $\text{Sb}_2\text{S}_5$ ).** This compound is prepared by conducting hydrogen sulfide into a solution of an antimonic compound:



It is a dark-orange, amorphous substance, insoluble in most liquids. It readily decomposes into the trisulfide and sulfur. Like the pentasulfide of arsenic, it dissolves in alkaline sulfides to form thio salts. The sodium salt  $\text{Na}_3\text{SbS}_4 \cdot 9 \text{H}_2\text{O}$ , known as Schlippe's salt, is readily obtained in crystalline form.

**Uses of antimony.** The chief use of antimony is in the preparation of alloys (see below), and especially the one known as Babbitt metal, which contains variable amounts of lead, tin, and antimony. Many alloys of antimony, like the element itself, expand on cooling, and this property makes them valuable for making castings in which fine lines are to be reproduced, as in the casting of type (see table, p. 485).

**Alloys.** Many elements, especially metals and metalloids, when melted together are mutually soluble, and on being cooled the solution freezes to a solid called an *alloy*. In the process of solidification one of three things may happen, depending upon the character of the components of the alloy: (1) the several elements present may each separate in minute crystals, making a fine-grained solid; (2) the crystals as they form may be solid solutions, each one being made up of all the elements present; (3) definite compounds may crystallize from the solution, together with crystals of the several elements. A great variety of properties is therefore to be found among the different alloys. It will be of interest to study the simplest of these three cases more closely.

**Eutectics.** In Chapter XII we found that when a solute is dissolved in a solvent the freezing point of the latter is lowered in proportion to the molecular concentration of the solute. We may employ a melted metal as the solvent and a second metal as the solute and find that the law of Raoult applies very well, the freezing point of the solvent metal being lowered. Consequently impure metals usually melt lower than pure ones.

If the two metals melt together in all proportions, the distinction between solvent metal and solute becomes arbitrary, and in any given case we regard the metal present in the larger proportion as the solvent. In general (but not always) each metal will lower the freezing point of the other. In the diagram (Fig. 150) let us indicate the composition of the alloy along the line  $AB$ , divided into 100 divisions. Let  $A = 100$  per cent antimony, and  $B = 100$  per cent lead.  $C$  will then represent 50 per cent of both, and  $E''$  80 per cent lead and 20 per cent antimony.

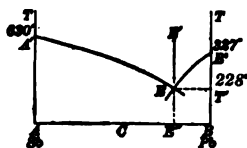


FIG. 150

The vertical lines  $AT$  and  $BT$  represent temperature,  $A'$  being the melting point of antimony and  $B'$  that of lead. If to pure lead we add a small percentage of antimony, the freezing point is lowered, the fall with increasing quantities of antimony being shown by the sloping line  $B'E$ . Similarly, if to pure antimony we add increasing quantities of lead the fall in freezing point is shown on the sloping line  $A'E$ . The point  $E$  ( $228^\circ$ ) is thus the lowest temperature at which any mixture of antimony and lead can remain liquid, and is called the *eutectic temperature*. The composition of the liquid at this point ( $E''$ ) is called the *eutectic composition*.

If we make a fusion of this composition ( $E'$ ) and cool the liquid to  $E$ , the two metals crystallize together in a very fine-grained solid, called the *eutectic*. This solid has the same composition as the liquid from which it deposits, but it is a mixture and not a compound. If we cool a fusion of any other composition, pure antimony or pure lead will crystallize out until the liquid comes to the composition  $E''$ , after which the eutectic will form.

The eutectic is therefore the lowest-melting mixture of the two elements. Most low-melting alloys are eutectics of two or more metals. Evidently we may have eutectics from fused salts, or oxides, or even with a salt and ice separating from aqueous solutions at low temperatures.

## BISMUTH

**Historical.** References to bismuth are found in the writings of the fifteenth century, but the element was confused with other metals, such as tin, antimony, and lead. Little was known of it with accuracy until the middle of the eighteenth century.

**Occurrence and preparation.** Bismuth is a rather rare element, yet it is found widely distributed in mineral regions both in this country and in parts of Europe, South America, and Australia. Most of the bismuth of the world comes from Bolivia. It usually occurs uncombined; but a great variety of rare minerals, especially sulfides, contain it as a constituent. The simplest of these are *bismuth glance* ( $\text{Bi}_2\text{S}_3$ ) and *bismuth ochre* ( $\text{Bi}_2\text{O}_3$ ).

A considerable quantity of the metal is produced from native bismuth by heating the ore and drawing off the liquid bismuth. It is produced from its compounds by rather complicated processes, the essential features of which are the preliminary roasting of the ore to produce the oxide, and the heating of this with carbon and a suitable flux. It is also obtained as a by-product in the refining of lead (p. 672).

**Properties and conduct.** Bismuth is a silvery metal with a decidedly ruddy tint. It is very crystalline, brittle, and has a high luster. It is difficult to prepare it in a perfectly pure condition, and its physical constants are therefore not accurately known. Its density is about 9.80, its melting point  $271^\circ$ , and its boiling point  $1420^\circ$ .

At ordinary temperatures bismuth is not affected by the air, but when heated it burns to form the trioxide  $\text{Bi}_2\text{O}_3$ . Like antimony, it decomposes steam in a reversible reaction. It dissolves in hot, concentrated sulfuric and nitric acids to form bismuth salts, but it is very slowly attacked by hydrochloric acid in the presence of air. The halogen elements combine directly with it, but not with great energy.

**Uses.** Bismuth is used chiefly in the making of alloys. Like antimony, the element, as well as its alloys, expands on cooling, and the alloys have low melting points. The table on the opposite page shows the approximate composition of the chief alloys of antimony and bismuth. Alloys of this kind are used in the manufacture of household utensils (Britannia metal), of type, of bearings in machinery (antifriction or Babbitt metal), and for liquid baths to secure a uniform temperature. The low

melting point of such alloys as Wood's metal (m. p. 60.5°) is turned to practical account in making automatic fire curtains and water sprinklers used in buildings as protection against fire, safety plugs in boilers, and many similar devices.

## ALLOYS OF ANTIMONY AND BISMUTH

	LEAD	TIN	ANTIMONY	BISMUTH	
Type metal (older) . .	50.0	25.0	25		Copper 3
Type metal (newer) . .	60.0	10.0	30		
Pewter . . . . .	20.0		80		
Britannia metal . . .		90.0	7		
Antifriction metal (Babbitt metal) . . .	66.0	17.0	17		Cadmium 12.5
Fusible metals:					
Rose's, m.p. 93.8° . .	25.0	25.0		50	
Wood's, m.p. 60.5° . .	25.0	12.5		50	
Newton's, m.p. 94.5° .	31.25	18.75		50	

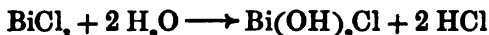
**Compounds of bismuth.** In nearly all of its compounds bismuth plays the part of a trivalent metal yielding a series of salts most of which are colorless. It forms no acids, as do the other members of the group. This is in accord with the general rule that as the atomic weight increases in any periodic family the metallic properties become more pronounced. The element forms no hydride.

**Oxides of bismuth.** While bismuth forms a number of oxides, including those having the formulas  $\text{BiO}$ ,  $\text{Bi}_2\text{O}_3$ ,  $\text{Bi}_2\text{O}_4$ , and  $\text{Bi}_2\text{O}_5$ , the trioxide alone is at all well known, and from it are derived most of the compounds of the element.

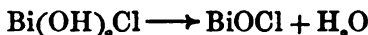
**Bismuth trioxide ( $\text{Bi}_2\text{O}_3$ ).** This is obtained by burning the metal or by heating the hydroxide or carbonate. It is a yellowish, crystalline powder melting at about 820° and volatile at very high temperatures. It dissolves in acids to form the corresponding salts, such as the chloride  $\text{BiCl}_3 \cdot 2\text{H}_2\text{O}$  and the nitrate  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ , both of which are colorless solids.

**Hydrolysis of bismuth salts.** While the normal salts are stable in solutions containing an excess of acid, they are hydrolyzed in water or even in dilute acids. In this hydrolysis a basic salt is

formed and not the hydroxide. With the chloride the reaction is expressed in the following equation:

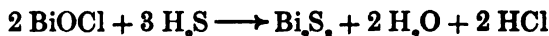


Such basic salts are nearly insoluble and, as a rule, lose water:



This oxychloride may be regarded as the chloride of the base  $\text{BiO} \cdot \text{OH}$ , in which the group  $\text{BiO}$  plays the part of a univalent radical. This radical is called *bismuthyl*, just as the corresponding antimony radical is called *antimonyl*. There are, therefore, two series of salts: the normal salts, corresponding to the formulas  $\text{BiCl}_3$  and  $\text{Bi}(\text{NO}_3)_3$ , and the bismuthyl salts, such as the chloride  $\text{BiO} \cdot \text{Cl}$ , the nitrate  $\text{BiO} \cdot \text{NO}_3$ , and the carbonate  $(\text{BiO})_2\text{CO}_3$ . A number of these bismuthyl salts, particularly the nitrate and the carbonate, are used in medicine. They are usually called bismuth subnitrate and bismuth subcarbonate.

**Bismuth sulfide ( $\text{Bi}_2\text{S}_3$ ).** The chief sulfide of bismuth has the formula  $\text{Bi}_2\text{S}_3$ . It can be prepared by direct union of the elements or by conducting hydrogen sulfide into a solution of a bismuth salt:



Prepared in this latter way it is a black, amorphous precipitate, insoluble in water, in dilute acids, and in the sulfides of sodium or ammonium.

### QUESTIONS

1. What elements have we studied that exist in more than one form?
2. The reaction between phosphorus trichloride and water belongs to what class of reactions?
3. Write the structural formula for phosphorus pentoxide, assuming that all the oxygen atoms are joined directly to the phosphorus and not to each other.
4. Write the equations for the reactions that take place when 1 molecule of phosphoric acid reacts with 1, 2, and 3 molecules respectively of sodium hydroxide.

5. A solution of disodium phosphate in water changes red litmus blue, notwithstanding the fact that it is an acid salt. Explain.

6. Write the equations for the reactions that take place when phosphorus tribromide and phosphorus tri-iodide are brought in contact with water. For what purpose are these reactions utilized (see Chapter XXI)?

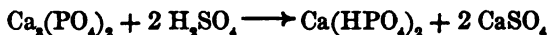
7. How do you reconcile the statement that antimony is below hydrogen in the electrochemical series with the statement that it liberates hydrogen from steam?

### PROBLEMS

1. A phosphate rock used as a source of phosphorus in the preparation of the element contained 80 per cent of calcium phosphate. Assuming that 10 per cent of the phosphorus is not liberated, what weight of the rock will be required to meet the needs of a plant preparing 50 tons of phosphorus monthly?

2. What weight of phosphorus is required to make 100 kg. of pure phosphoric acid (hydrogen phosphate)?

3. In the manufacture of fertilizers what weight of 50 per cent sulfuric acid is required for the treatment of 1 ton of phosphate rock containing 80 per cent calcium phosphate, assuming that the reaction is as follows:



4. A compound, upon analysis, was found to have the following composition: Ca, 38.74 per cent; P, 20.01 per cent; O, 41.24 per cent. Calculate its formula.

5. What weight of stibnite is necessary to furnish sufficient antimony to make 100 kg. of Babbitt metal?

6. What weight of bismuth subnitrate can be prepared from 100 g. of bismuth?

7. How much heat is evolved in converting 100 g. of  $\text{PCl}_5$  into  $\text{PCl}_3$ ?

8. Calculate the atomic ratio of the elements present in Wood's metal.

## CHAPTER XXX

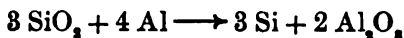
### THE SILICON FAMILY AND BORON

**Introduction.** In both families of Group IV of the periodic table, the elements of small atomic weight are acid-forming in character and resemble carbon in many particulars, but with increase in atomic weight they become metallic in their properties. It is therefore convenient to describe the acid-forming elements, silicon, titanium, and zirconium, at this point, reserving the more metallic elements for a subsequent chapter. It will be appropriate to describe the element boron in connection with silicon, since it also has acid-forming properties, while the other members of the third group are metallic in character.

#### SILICON

**Occurrence.** Next to oxygen, silicon is the most abundant element. Neither the element nor its compounds are found in the air, nor to any considerable extent in water, but the solid crust of the earth is estimated to contain 27.74 per cent of silicon. All varieties of granite, gneiss, sandstone, shale, clay, and marl contain large percentages of the element, limestone and dolomite being the only important geological formations measurably free from it. In the realm of inorganic nature it is the central element just as carbon is of fundamental importance in organic nature. To some extent its compounds are assimilated by plants and animals, and they constitute the outer shell of many aquatic organisms.

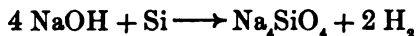
**The element.** In the laboratory, crystallized silicon is best prepared by the reduction of the dioxide with aluminium powder:



The silicon dissolves in the excess of melted aluminium, and when the solution has cooled and become solid, the aluminium is dissolved in hydrochloric acid, the silicon being left in the form of shining metallic needles. The reduction of the dioxide with carbon has always presented the difficulty that the reduced element tends to combine with excess of carbon to form a carbide. This difficulty has been overcome to a large extent, and nearly pure silicon is now manufactured in large quantities. By reducing a mixture of the oxides of silicon and iron with carbon, an alloy of the two elements called *ferrosilicon* is obtained. This alloy, as well as the purer silicon, finds an important application in the metallurgy of iron and will be referred to in that connection.

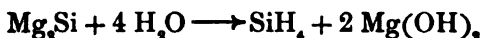
**Properties.** The element presents a close analogy with carbon in that it can be obtained in amorphous form, as well as in crystals of the isometric system, resembling diamond. The crystals are very hard, easily scratching glass, and have a density of 2.35. They melt at 1420°. A lump of the element is very brittle and breaks with a crystalline fracture, which has a metallic, silvery appearance.

**Chemical conduct.** Silicon is readily attacked by the halogens, forming gaseous compounds. The gaseous halogen hydrides attack it at red heat, with evolution of hydrogen. The alkalis dissolve it, evolving hydrogen and forming soluble silicates — a reaction sometimes used in the commercial preparation of hydrogen:

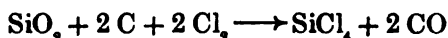


Water containing a trace of alkalis acts slowly upon it in a similar way. It is not attacked by oxygen as easily as would be expected, considering the difficulty with which its oxide is reduced. This inactivity is due to its high melting point and to the fact that a thin film of nonvolatile oxide forms upon the surface, which protects it from further action. At high temperatures it combines with the great majority of elements, forming *silicides* such as those of magnesium ( $\text{Mg}_2\text{Si}$ ) and carbon ( $\text{CSi}$ ).

**Halogen and hydrogen compounds of silicon.** A large number of compounds of silicon with hydrogen and the halogens have been prepared, and they are of interest as showing the close relationship of the element with carbon. The hydrides are formed by the action of acids or water upon a suitable silicide, just as are those of carbon ( $C_2H_2$ ) and sulfur ( $H_2S$ ):



The halogen derivatives are formed by direct union of silicon with the halogens, or by conducting the halogen vapor through a heated mixture of carbon and silicon oxide:



The following table will serve to show the melting point and boiling point of a number of these silicon compounds together with those of the corresponding carbon compounds.

TABLE OF SOME CARBON AND SILICON COMPOUNDS

FORMULA	MELTING POINT	BOILING POINT	FORMULA	MELTING POINT	BOILING POINT
$CH_4$ . . . . .	- 184.0	- 164.0	$SiH_4$ . . . . .	- 200.0	
$C_2H_2$ . . . . .	- 171.4	- 85.4	$Si_2H_6$ . . . . .	- 138.0	52.0
$CCl_4$ . . . . .	- 23.8	76.7	$SiCl_4$ . . . . .	- 102.0	59.0
$C_2Cl_4$ . . . . .	187.0		$Si_2Cl_6$ . . . . .	- 1.0	146.0
$C_3Cl_8$ . . . . .	160.0	268.0	$Si_3Cl_8$ . . . . .	- 12.0	210.0
$CBr_4$ . . . . .	92.5	189.5	$SiBr_4$ . . . . .	- 12.0	153.0
$Cl_4$ . . . . .	decomp.		$SiI_4$ . . . . .	120.5	290.0 $\pm$
$CF_4$ . . . . .		- 15.0	$SiF_4$ . . . . .	- 102.0	sublimes
$CHF_3$ . . . . .		20.0	$SiHF_3$ . . . . .	- 110.0	30.2
$CHCl_3$ . . . . .	- 60.3	61.3	$SiHCl_3$ . . . . .	- 134.0	33.0
$CHBr_3$ . . . . .	9.0	146.0	$SiHBr_3$ . . . . .	- 60.0	115.0
$CHI_3$ . . . . .	119.0	decomp.	$SiHI_3$ . . . . .	8.0	decomp.

**Silicon chloride ( $SiCl_4$ ).** This is a colorless liquid which boils at  $59^\circ$  and hydrolyzes in contact with air, forming hydrochloric acid and an oxide or hydroxide of silicon. It can be made by the general method given above. During the World War large quantities were prepared by the action of chlorine on silicon

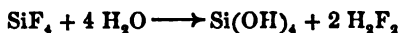
carbide ( $\text{SiC}$ ) and used to produce smoke clouds for concealing troops and ships. For the production of smoke it is best used in connection with ammonia, which combines with the hydrogen chloride produced by the hydrolysis of the silicon chloride in moist air, forming dense white clouds of ammonium chloride.

**Silicon fluoride ( $\text{SiF}_4$ ).** Silicon fluoride is a gas at ordinary temperature, and is easily prepared by the action of hydrofluoric acid upon silicon dioxide :



In a somewhat similar way hydrofluoric acid acts upon silicates, converting both the silicon and the metals into fluorides.

**Fluosillicic acid ( $\text{H}_2\text{SiF}_6$ ).** When silicon fluoride is conducted into water, it is decomposed according to the following equation :



A part of the silicon hydroxide then dissolves in the hydrofluoric acid :



The soluble product  $\text{H}_2\text{SiF}_6$  is called fluosillicic acid. It is a moderately strong acid and forms soluble, well-crystallized salts with most of the metals. The potassium salt  $\text{K}_2\text{SiF}_6$  is very sparingly soluble, so that the acid is frequently employed as a test for potassium. Most of those elements which in the free state resemble metals, but whose chemistry is that of nonmetals, form fluo acids of the same general kind. Among these are all the elements in this group except carbon.

#### Preparation of fluosillicic acid.

A dilute solution of fluosillicic acid is conveniently prepared by the use of the apparatus shown

in Fig. 151. A mixture of sand ( $\text{SiO}_2$ ) and powdered fluorspar is placed in the flask *A*, and concentrated sulfuric acid is added. The hydrofluoric acid liberated acts upon the sand, forming silicon tetrafluoride. This is conducted through a wide delivery tube *B* into a beaker of water, provided

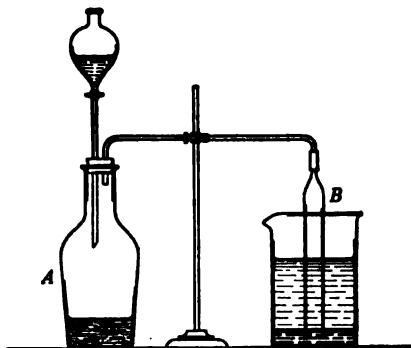


FIG. 151

with a layer of mercury on the bottom, into which the delivery tube dips. This is to prevent the solid silicic acid which also forms from clogging the tube. At the close of the operation the silicic acid is filtered off. The filtrate contains the fluosilicic acid in solution.

**Silicon dioxide (silica) ( $\text{SiO}_2$ ).** Although several oxides of silicon have been described, the dioxide  $\text{SiO}_2$ , called *silica*, is the only one which is at all well characterized. Practically all the silicon of nature occurs either as the dioxide itself or as its derivatives, so that it is a most important substance. As found in nature, silica is usually in the crystalline variety known as *quartz*. It forms beautiful colorless crystals belonging to the hexagonal system, which are sometimes of great size. A single one found in California weighed over a ton. These crystals are frequently tinted by impurities, producing smoky and milky quartz and

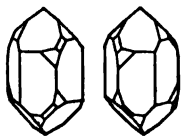


Fig. 152

amethyst. An examination of well-formed crystals shows that they are not symmetrical but are rights and lefts like a pair of gloves. Fig. 152 shows such a pair. Above  $800^\circ$  quartz changes into two other forms, known as *tridymite* and *cristobalite*, and there are several other

crystal forms known. Quartz is a constituent of many conglomerate rocks, such as sandstone. Silica also occurs in amorphous form, usually impure and often partially hydrated. Among such forms are *flint* and *opal*. It also acts as the binding material which unites the several minerals constituting *granite* and *gneiss*.

Quartz has a density of 2.66 and is hard enough to scratch glass and most metals. It is therefore used for grinding and polishing purposes. Silica is very difficult to melt, but at the temperature of the oxyhydrogen blowpipe it softens to a viscous liquid resembling melted glass, which can be drawn into threads or fashioned into laboratory utensils, such as crucibles or flasks, which have many desirable qualities. They are not attacked by most reagents, and, owing to the fact that silica has a very small coefficient of expansion with temperature, such vessels can be heated to redness and plunged into water without danger of cracking.

**The melting point of crystallized silica.** Silica is undoubtedly a very highly crystalline substance, yet it would appear to have no sharp melting point but to pass by insensible stages into a viscous liquid. On cooling, this gradually hardens without resuming a crystalline structure. This conduct does not seem to be in accord with the general principles already developed concerning the melting point of crystals (p. 98), but the explanation is really very simple. The melted silica is so viscous that it retains the form of the original solid, and this amorphous liquid, on further heating, gradually softens. On cooling, the viscous liquid permanently supercools and, as a rule, fails to crystallize again. By optical observations it has been shown that the true melting point is about 1600°.

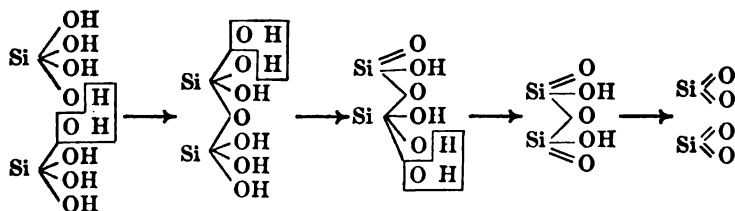
**Acids of silicon.** Like carbon dioxide, silica is an acid anhydride, and this, together with its action with hydrofluoric acid, constitutes its most interesting chemical property. In combination with water it forms not only one but a considerable variety of acids.

**Orthosilicic acid ( $\text{H}_4\text{SiO}_4$ ).** Since silicon is quadrivalent, its normal hydroxide would have the formula  $\text{Si}(\text{OH})_4$ . This appears to be a quadribasic acid, for salts such as  $\text{Ca}_2\text{SiO}_4$  and  $\text{KAlSiO}_4$  are well known. This hydroxide is called *orthosilicic acid*, the formula being written  $\text{H}_4\text{SiO}_4$ , and its salts are called orthosilicates.

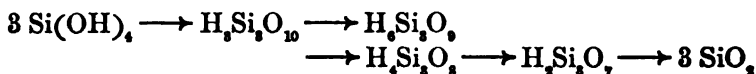
**Metasilicic acid ( $\text{H}_2\text{SiO}_3$ ).** Orthosilicic acid readily loses one molecule of water:  $\text{H}_4\text{SiO}_4 \longrightarrow \text{H}_2\text{SiO}_3 + \text{H}_2\text{O}$

The acid so formed is analogous to carbonic acid ( $\text{H}_2\text{CO}_3$ ) and is called *metasilicic acid*. Its salts are called metasilicates, the sodium and calcium salts having the formulas  $\text{Na}_2\text{SiO}_3$  and  $\text{CaSiO}_3$ .

**Condensed acids.** Orthosilicic acid may also lose water by the coöperation of more than one molecule. This may be understood best by reference to the following structural formulas:



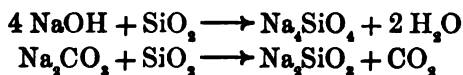
With three molecules we might have, in a similar way,



When two or more molecules of an acid lose water in this way, forming products such as the ones represented above, the resulting acids are called *condensed acids*, or *polyacids*, the ones just formulated being *polysilicic acids*. To a greater or less extent this tendency is observed with nearly all oxygen acids, and we have already had illustrations in the pyro acids of phosphorus and arsenic.

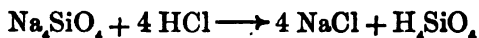
In the case of silicon this tendency is very pronounced, and most of the natural silicates are salts of condensed acids. While there is no doubt as to the existence of these various acids, none of them, not even the ortho or meta acids, have been prepared in pure form. They all gradually lose water and pass finally into the dioxide.

**The silicates.** Almost all the silicates, whether salts of simple or of condensed acids, are insoluble in water, excepting those of sodium and potassium. The latter may be prepared by fusing pure silica with sodium hydroxide or carbonate:



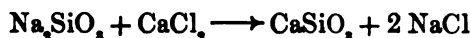
A solution of the products of such fusions in water is called *water glass*. It doubtless contains a mixture of the various silicates of sodium or potassium. When the solution is evaporated, it forms a thick liquid, which gradually hardens into a glass. It is used as a cement or glue for many purposes; also in preserving eggs.

When a concentrated solution of water glass is treated with an acid such as hydrochloric acid, silicic acid is liberated as a jellylike mass:

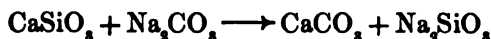


This jelly will be discussed in detail in the following chapter.

When salts of the various metals are added to a solution of sodium silicate, the insoluble silicates are precipitated:



Most natural silicates when fused with sodium carbonate are decomposed, and sodium silicate is formed:



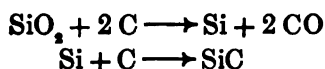
The melted sodium carbonate forms a liquid in which the silicates are soluble but the carbonates are not. The insoluble carbonate is therefore precipitated. When the melt is cooled and digested with water, the sodium silicate dissolves, while the carbonate and oxides of the other metals are left undissolved. They may be filtered off and dissolved in acids. Such fusions are very frequently resorted to in chemical analysis as a means of decomposing the silicates and getting their constituents into solution, as many of them are not attacked by acids.

**Varieties of natural silicates.** Some natural silicates are salts of metasilicic acid; others are derived from orthosilicic acid. Still more frequently they are salts of various polysilicic acids. These are designated by prefixes, such as *di-* and *tri-*, according to the number of molecules of the orthosilicic acid which have been condensed. The disilicic acid  $\text{H}_2\text{Si}_2\text{O}_7$  and the trisilicic acid  $\text{H}_4\text{Si}_3\text{O}_{10}$  are the most common of these. Very often, when the acid has as many as four hydrogen atoms, two or more different metals replace the hydrogen, forming mixed salts, such as  $\text{KAlSiO}_3$  (mica) or  $\text{KAlSi}_3\text{O}_8$  (feldspar). The following table will illustrate these types of silicates:

VARIETIES	ACIDS	SALTS	MINERALS
Metasilicates	$\text{H}_2\text{SiO}_3$	$\text{CaSiO}_3$	Wollastonite
Orthosilicates	$\text{H}_4\text{SiO}_4$	$\begin{Bmatrix} \text{Mg}_2\text{SiO}_4 \\ \text{Zn}_2\text{SiO}_4 \end{Bmatrix}$	Olivine Willemite
Disilicates	$\begin{Bmatrix} \text{H}_2\text{Si}_2\text{O}_7 \\ \text{H}_4\text{Si}_2\text{O}_6 \end{Bmatrix}$	$\begin{Bmatrix} \text{Mg}_3\text{Si}_2\text{O}_7 \\ \text{KAlSi}_2\text{O}_6 \end{Bmatrix}$	Serpentine Leucite
Trisilicates	$\text{H}_4\text{Si}_3\text{O}_{10}$	$\begin{Bmatrix} \text{KAlSi}_3\text{O}_8 \\ \text{NaAlSi}_3\text{O}_8 \end{Bmatrix}$	Orthoclase Albite

**Fusion of the silicates.** Some of the silicates have a sharp melting point and recrystallize on cooling. Many of those with a relatively low melting point resemble silica in that they fuse into a viscous liquid which, on cooling, hardens without crystallizing. If several different silicates are melted together, they mix freely to a homogeneous liquid. Crystals of definite composition may separate from the melt when it is cooled, but more frequently the liquid solution simply becomes more and more viscous, until it is as rigid as a true solid. Such products are called *glasses*, and they are to be regarded as very viscous solutions of one silicate in another. The industry of glass making will be referred to in a subsequent chapter.

**Silicon carbide (carborundum) (SiC).** When sand, coke, and a little sodium chloride are heated in an electric furnace, the silica is reduced, the resulting silicon combining with carbon to form a carbide:



After the reaction the carbide is found in the form of beautiful crystal plates, which are colorless when pure, but are usually a brilliant iridescent purple, the color being largely due to optical rather than to chemical causes. The material is almost as hard as diamond and is much used in place of emery for grindstones and polishing powders. Although its heat of combustion is great, amounting to 288,800 cal., it is extremely inactive chemically except at very high temperatures. It then acts as a strong reducing agent, both of the constituent elements being converted into oxides.

**Commercial production of carborundum.** Carborundum is made on a large scale at Niagara Falls. The furnace in which it is prepared is quite similar to the one employed in the manufacture of graphite (p. 187). It is built out of loose brick and half filled with the charge. The electrodes are put in place, a layer of pieces of carbon spread between them, and the charge filled in to the top. A cross section of a furnace so charged is represented in Fig. 153. *A* is the core of carbon, *B* the mixture of materials. The broken carbon offers great resistance to the current, and the heat along

the carbon core becomes very intense. This causes reaction to take place from the center for some distance into the mass, the result being represented in Fig. 154.

*A* is the core of carbon surrounded by a core of crystallized carborundum *B*, and this in turn by a layer *C* of amorphous carborundum and partially reduced products. These are known as *white stuff*,

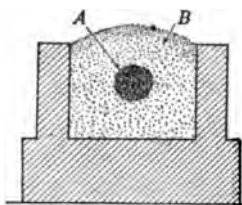


FIG. 153

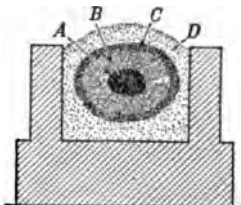


FIG. 154

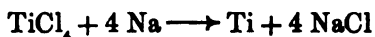
*silozicon*, or *silundum*, according to their character. They are useful for making furnace linings and fire brick. The material *D* is unchanged.

**The silicate industries.** A number of most important industries are based upon the silicates and the chemical transformation which they undergo. The oldest of these are the various ceramic industries, including the making of bricks, tile, terra cotta, dishes, porcelain, and glass. Glass making, with its many details, is, from a chemical standpoint, very closely associated with the making of porcelain and the glazing of clay vessels. Cement making also involves similar chemical principles. These three great industries are sometimes collectively spoken of as the *ceramic industries*, and their discussion would naturally take place in the present chapter, but since all these industries are based on the conduct of metallic silicates, it seems best to delay the discussion until a number of the metals have been studied, especially sodium, calcium, and aluminium.

## TITANIUM

**Occurrence.** Titanium is really very abundant in nature but is nowhere concentrated in large deposits. Its chief ores are *rutile* ( $\text{TiO}_2$ ) and *ilmenite* ( $\text{FeTiO}_3$ ). Our supply of these ores comes almost entirely from Virginia. In small amounts titanium is widely distributed, as is shown by the fact that out of 800 igneous rocks analyzed in the laboratory of the United States Geological Survey 748 contained titanium. It is also found as a variable constituent of certain iron ores known as *titanic iron ores*.

**Preparation and properties.** The element can be obtained by the reduction of the dioxide with carbon in an electric furnace, but prepared in this way it always contains carbon and usually nitrogen. Very pure specimens have been prepared by the action of titanium chloride on sodium in a closed steel bomb:



When the element contains carbon it is hard and very brittle. Its melting point is above that of platinum, being about 1800°. Its specific gravity is 4.5.

An alloy known as *ferrotitanium* is made by reducing with carbon iron ores rich in titanium. This alloy is manufactured on a large scale at Niagara Falls and is used in preparing titanium steel. An average sample of this alloy contains 15.5 per cent of titanium, 1.4 per cent of silicon, 7.5 per cent of carbon, and 74.3 per cent of iron.

**The compounds.** The dioxide of titanium, like that of silicon, is an acid anhydride and forms a large number of acids closely resembling the various types of silicic acids. These are even weaker than those of silicon, and their salts hydrolyze more readily. Fluotitanic acid ( $\text{H}_2\text{TiF}_6$ ) and its salts are well known.

Unlike silicon, titanium also forms salts in which the element acts as a tervalent metal. The titanic salts are formed by the action of nascent hydrogen upon derivatives of the dioxide. The sulfate  $\text{Ti}_2(\text{SO}_4)_3$  and the chloride  $\text{TiCl}_3 \cdot 6 \text{H}_2\text{O}$  are examples. These salts are either green or violet in color.

At high temperatures titanium shows a very marked tendency to unite with nitrogen, the nitride  $\text{TiN}$  being the product of this direct union. The nitride is therefore always produced in any attempt to prepare titanium in an apparatus to which air has access, and this compound was formerly considered to be the element itself. When the iron ores containing titanium are reduced, a substance resembling crystallized copper is often found in the slag or adhering to the lining of the furnace. This was at one time supposed to be the metal, but is now recognized to be a

compound containing variable amounts of titanium, carbon, and nitrogen, known as *titanium carbonitride*. It was prepared on a large scale during the World War and used in the manufacture of *titanium tetrachloride* ( $\text{TiCl}_4$ ). This chloride is a liquid, boiling at  $138^\circ$ , and, like silicon tetrachloride, hydrolyzes in contact with moist air, evolving dense clouds. It was employed for the production of smoke clouds in the war, but was inferior to both silicon tetrachloride and phosphorus for this purpose. Certain compounds of titanium, especially the white powdered dioxide, are used to a limited extent in paints, and may come into more general use.

### ZIRCONIUM

**Occurrence and preparation.** This is a rather rare element which occurs in nature as the oxide  $\text{ZrO}_2$ , either combined with silica to form the well-crystallized orthosilicate  $\text{ZrSiO}_4$ , which constitutes the mineral *zircon*, or associated with other oxides, especially those of iron and silicon, in the mineral *baddeleyite*. Some forms of zircon are clear white, others are tinted different shades of yellow or red and are used as semiprecious stones under the name *hyacinth*.

Zirconium deposits are found in North Carolina and Florida in the United States, and in Norway and Brazil. In the latter country there is a large deposit of free zirconium oxide, known as *zirconia*, which is extensively mined. The free element can be prepared by methods similar to those used in the case of titanium. An alloy of iron and zirconium, known as *ferrozirconium*, has been prepared, but the free element has as yet very limited uses.

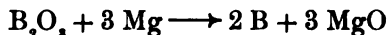
**Compounds and uses.** While zirconium forms acids similar to those of silicon and titanium, particularly the fluozirconic acid ( $\text{H}_2\text{ZrF}_6$ ), its metallic properties are much more developed and it forms many salts in which the element plays the part of a quadrivalent metal like tin. The hydroxide  $\text{Zr}(\text{OH})_4$  has very feeble basic properties, however, and the partial anhydride  $\text{ZrO}(\text{OH})_2$  is the base from which most of the salts are derived. Thus we have many such salts as zirconyl chloride,  $\text{ZrOCl}_2$ . As an element it is therefore intermediate between the acid-forming elements of this group and those which are more distinctly metals. Its most important compound is the dioxide  $\text{ZrO}_2$ , which is one of the most refractory oxides known, fusing at about  $3000^\circ$ . It is used in the manufacture of certain utensils, such as crucibles, which have to withstand a high temperature. It is made into bricks and sold under the name of *zircite* for use in lining furnaces. It has also been used in making enamels and white opaque glass.

## BORON

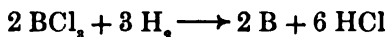
**Introductory.** The tervalent element boron finds a place as the first member of Group III of the periodic classification, but in its properties, as well as in those of its compounds, it is much more closely related to silicon than to the tervalent elements. Since it is tervalent, the formulas of its compounds differ from those of silicon.

**Occurrence.** Boron occurs in the form of boron hydroxide, known as boric acid ( $B(OH)_3$  or  $H_3BO_3$ ), in many hot springs, particularly in Italy. In the form of borax ( $Na_2B_4O_7$ ) it is found in limited amounts in the desert regions of California and Nevada, and in larger amounts in Peru and Chile. The most important deposit of boron in the United States is in California, where it is found in the form of the calcium salt of a complex boric acid, which has the formula  $Ca_2B_6O_{11} \cdot 5 H_2O$  and is known as *colemanite*. This deposit now serves as the source of practically all the boron compounds used in the United States. In Chile, boron occurs chiefly in the form of *boronatocalcite* ( $Na_2B_4O_7 \cdot 2 CaB_4O_7 \cdot 18 H_2O$ ).

**Preparation and properties.** Boron has an extraordinary affinity for oxygen, so that the oxide is very difficult of reduction. By heating it with magnesium powder an impure product may be obtained which always contains either magnesium or oxygen:



The pure element has been obtained by Weintraub by the action of hydrogen upon boron chloride at the temperature of the electric arc:



So prepared the element is gray and shows no crystalline structure. It melts above  $2200^\circ$ , but has a considerable vapor pressure as low as  $1600^\circ$ . In hardness it closely approaches the diamond. It is remarkable for the extraordinary extent to which its electrical resistance falls off with rise in temperature.

**Boric oxide ( $B_2O_3$ ).** While many compounds of boron have been made, the oxide and its derivatives are the most important. The only oxide definitely known is boric oxide ( $B_2O_3$ ). This is obtained by heating the hydroxide to fusion, in the form of a transparent glass. By the partial reduction of boric oxide a product is obtained called *boron suboxide*. It is used in casting copper, as its addition to the melted metal prevents the formation of blowholes on cooling. The principal use of boric oxide is in making glass.

**Boric acid ( $H_3BO_3$ ).** This compound is found dissolved in the water of hot springs in some localities, particularly in Italy. Being volatile with steam, boric acid is present in the vapor from these springs. The acid is easily obtained from these sources by condensation and evaporation, the necessary heat being supplied by other hot springs. It is often prepared by treating a hot solution of borax ( $Na_2B_4O_7$ ) with sulfuric acid. Boric acid, being but sparingly soluble in water, crystallizes on cooling:

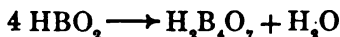


Boric acid crystallizes in pearly flakes, which are slippery to the touch. It is a mild antiseptic and is sometimes used in medicine. Its acid properties are extremely weak.

**Metaboric acid and tetraboric acid.** When boric acid is gently heated, it is converted into metaboric acid ( $HBO_2$ ):

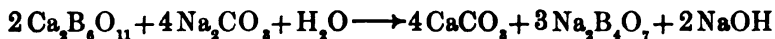


On heating metaboric acid to a somewhat higher temperature, *tetraboric acid* ( $H_2B_4O_7$ ) is formed:

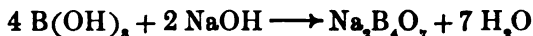


**Borax ( $Na_2B_4O_7$ ).** While salts of metaboric acid are known; most of the borates are derived from condensed acids, as indicated by the formulas for borax,  $Na_2B_4O_7$ , and colemanite,  $Ca_2B_6O_{11} \cdot 5 H_2O$ . Of these salts, borax is by far the most important. As is indicated by its formula, its chemical name is *sodium*

*tetraborate*. Formerly considerable borax was obtained from the natural deposits found in desert regions in the western states, but at present the entire amount obtained in the United States, amounting to about 100,000 tons annually, is made from colemanite. Borax is obtained from colemanite by treatment with sodium carbonate:



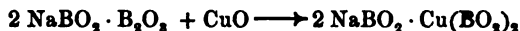
It is also formed when boric acid is treated with sodium hydroxide:



When crystallized from water at ordinary temperatures, borax separates in the form of prismatic crystals having the formula  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10 \text{H}_2\text{O}$ . If crystallized at a temperature above  $60^\circ$ , it separates in the form of octahedrons, having the formula  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 5 \text{H}_2\text{O}$ . The prismatic form is the common one. In solution borax is strongly hydrolyzed and has an alkaline reaction. It is often used in place of soap in household cleaning and for softening hard water.

When the crystallized salt is heated, it swells up to a sort of froth, loses its water of crystallization, and then fuses to a clear glass. This glass readily dissolves various metallic oxides and acquires characteristic colors from them (see metaphosphates, p. 470). This property is turned to account in chemical analysis in testing for the presence of certain metals. Owing to this same property it is used as a flux in brazing or hard soldering. It dissolves all the metallic oxides which coat the surfaces of the metals to be joined, and produces a clean surface to which the solder will adhere.

If it is remembered that borax contains an excess of acid anhydride, which will be more readily seen if its formula is written  $2 \text{NaBO}_2 \cdot \text{B}_2\text{O}_3$ , it is easy to understand its solvent action on metallic oxides. They unite with this excess of acid, as indicated in the equation



The polysilicates would serve the same purpose if they melted at a sufficiently low temperature. Some of the glasses formed in this way are useful in the process of covering ironware with enamels, since they are well adapted to binding the enamel to the iron, and they are often an ingredient of the enamel itself. This use constitutes one of the chief applications of borax.

## QUESTIONS

1. (a) Ordinary feldspar (p. 495) is a salt of what acid? (b) Show how this acid may be regarded as derived from orthosilicic acid.
2. Would you expect salts of tetraboric acid to hydrolyze? Explain.
3. (a) Write the equation for the hydrolysis of silicon tetrachloride. (b) Compare with the equation for the hydrolysis of phosphorus trichloride.
4. (a) Colemanite is a salt of what acid? (b) Show the relation between this acid and boric acid.
5. Why is it that heating silica with carbon sometimes produces silicon and at other times carborundum?

## PROBLEMS

1. Which contains the greater per cent of silicon, mica or feldspar?
2. What weight of carbon is necessary to react with silica in the preparation of one ton of carborundum?
3. What weight of colemanite is necessary for the preparation of 100 kg. of ordinary borax?
4. Calculate the weight of ordinary borax obtained by crystallizing 100 kg. of the anhydrous sodium tetraborate at ordinary temperatures.

## CHAPTER XXXI

### COLLOIDS

**Introduction.** If we shake a bottle containing coarse sand and water and then set it aside, the sand quickly settles to the bottom. The finer the sand is powdered, the longer the time required for settling. If we could grind the sand to individual molecules and then shake them with water, we should have a true solution that would not settle because of the energy of motion of the molecules.

It would seem probable that long before subdivision into individual molecules had been reached, we should have particles so small that when shaken with water the resulting mixture would possess characteristics different from those either of an ordinary suspension or of a true solution. A mixture of this kind, intermediate between a suspension and a true solution, is called a *colloidal suspension*, or often a *colloidal solution*, and the solid material so scattered, or *dispersed*, is said to be a *colloid*, or in *colloidal condition*.

**Brownian movement.** As early as 1827 the English botanist Brown, while examining microscopically fine grains of pollen suspended in water, noticed that they kept up a curious zigzag motion which became known as the *Brownian movement*; but the cause of this motion remained unexplained for fifty years. It was then recognized to be a necessary consequence of the kinetic energy of the molecules of the solution. For, if these molecules have the high speed we have calculated for them, their collisions with exceedingly fine particles will impart very considerable and erratic motions to those particles, even though the latter are many times as heavy as the molecules striking

them. It is clear that this Brownian motion will never stop, which accounts for the fact that colloidal solutions do not settle as suspensions do.

**Tyndall effect.** As a striking lecture experiment the English physicist Tyndall showed that many liquids which appeared to be perfectly clear and even colorless, could be proved to contain a great deal of finely suspended matter incapable of removal by ordinary filtration. It is only necessary to pass a strong beam of light through the liquid (in a dark room). In the absence of suspended matter the beam of light has no visible path through the liquid; but the presence of suspended matter at once occasions a bright path through the liquid (Fig. 155), like the path of a sunbeam through the dusty air of a dark room. The light is diffracted by the solid particles, each

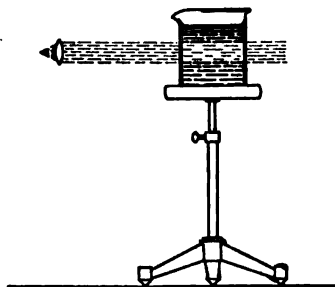


FIG. 155

of which becomes a visible source of light, even when too small to be seen directly by a microscope. This bright path of light through a liquid is called the *Tyndall effect*.

**Ultramicroscope.** The German chemist Zsigmondy has perfected an instrument called the *ultramicroscope* that greatly magnifies this Tyndall effect. Its essential parts are a small cubical cell of glass or quartz to hold the liquid; a powerful source of light to send a pencil of rays through the liquid; and a good microscope so mounted as to look upon the liquid at right angles to the beam of light against a dark background. The minute particles in the liquid are seen as bright specks of light in rapid motion, like motes in a sunbeam.

**Size of colloidal particles.** Evidently we may have in suspension particles of a wide range in size. When we pass below a rather definite size the suspension begins to acquire the properties we associate with colloids, and when we go below another rather

arbitrary point the suspension begins to act more like a solution. To indicate such small sizes the millimeter is too large a unit of length, and one millionth of a millimeter is employed as a standard. This is called a *millimicron* and is designated by the symbol  $\mu\mu$ , which is the Greek for *mm*. In a general way it may be said that particles that range in diameter between  $100\ \mu\mu$  and  $0.1\ \mu\mu$  act as typical colloids, but any such limits are purely arbitrary. The smallest particles we can see with the ultramicroscope probably contain at least  $(60)^*$  or  $(70)^*$  molecules.

**Dispersed systems.** We have already seen some resemblance between a colloid in liquid suspension and dust particles in the air. When the particles in the air are numerous enough we call it *smoke*. In a similar way a very fine suspension of droplets of water in air is called *fog*; droplets of liquid scattered through a second liquid constitute an *emulsion*; minute bubbles of a gas in water constitute *foam*. All of these have the structure that characterizes colloids in that they consist of one form of matter in a very fine state of division scattered through a second form. The general term *dispersed systems* is employed to designate all such cases, irrespective of the physical state of the materials, the term *colloid* being reserved for a solid dispersed in a liquid.

**Methods of preparation.** The various methods for preparing colloids may all be classified as depending upon one of two general principles.

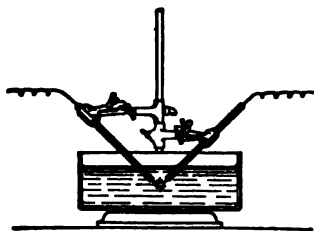


FIG. 156

1. **Dispersion methods.** One principle is to subdivide a solid until the process results in particles of colloid size. This is called *dispersion*. In the case of some of the metals this can be accomplished by bringing the ends of two stout wires of the metal close together under

water and passing an electric current through the wires so as to form an arc between their ends (Fig. 156). Particles of the metal are torn off from the wires, and some of the metal is

probably volatilized and condensed as a smoke. The solid particles remain suspended as a colloid and impart characteristic colors to the liquid. Metals above hydrogen in the electrochemical series cannot be used with water as the dispersion medium, but can be used with other solvents.

**2. Condensation methods.** We may start with substances in solution or in the gaseous state and bring about the production of a solid in finely divided form. For example, we may pass hydrogen sulfide into a neutral solution of a compound of antimony (tartar emetic) and produce colloidal antimony sulfide ( $\text{Sb}_2\text{S}_3$ ); or we may add an acid to a dilute solution of sodium thiosulfate and produce colloidal sulfur; or we may prepare a very dilute solution of gold chloride and add a reducing agent, such as ferrous sulfate or hydrazine chloride, producing colloidal gold.

It will be seen that all these processes result in gathering the particles together into clumps of colloidal size. The process must then stop; for if it continues too far, the clumps will be too large and will form a precipitate. Some chemists think that the formation of a colloid is always the first step in precipitation; it is also thought by some that crystals are formed from colloids, the haphazard clumps of colloids serving as piles of building materials out of which the orderly crystals are built up.

**Optical properties.** A typical colloidal solution usually looks clear, though it may be highly colored. As we have seen, it looks opaque when illumined by a strong beam of light. When placed in such a position that light is reflected from the solution to the eye, the solution often looks fluorescent or even muddy and turbid, while perfectly clear by transmitted light.

The color is no indication of the materials present, for the color depends chiefly upon the size and uniformity of the particles. We may have colloidal solutions of gold of almost any color, the smallest particles giving a red, and the coarser ones a purple color, with intermediate greens and blues. These colors are usually very intense considering the extremely small amount of solid present, so that even highly colored solutions may almost

defy chemical analysis to determine the coloring matter. Many colored glasses, especially the ruby-red glasses colored by copper, gold, or selenium, owe their intense color to colloidal dispersions of these elements or their oxides in the glass. The color of many precious gems is probably due to colloidal material.

**Dialysis.** If we filter a colloidal solution through even the best of filter paper, no solid is retained on the paper. If we use a fine parchment paper, or an animal membrane, we find that the colloid is now prevented from

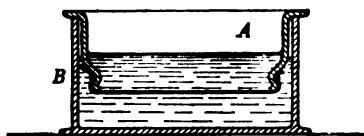


FIG. 157

passing through the filter. By taking advantage of this fact we may purify a colloidal solution from dissolved electrolytes by a process called *dialysis*. The membrane is stretched on a frame like a tambourine, constituting a *dialyzer* (Fig. 157). The colloidal solution *A* is placed in it, and

is partially immersed in pure water *B*. The impurities that are in real solution diffuse through the membrane, while the colloids do not, and are thus purified.

**Electrical charge.** Colloidal solutions have been found to have a very small osmotic pressure, and the freezing point and boiling point differ little from those of the pure solvent, all of which indicates very large assemblages of molecules in the colloid particles. If we try the electrical conductivity of colloid solutions, we find it to be rather larger than we should expect, though still much smaller than that of a real solution of equivalent concentration.

The colloid particles do not seem to dissociate into two kinds of ions, but the whole particle appears to move to one or the other electrode. Some colloids are charged positively, including most of the metallic hydroxides; others are charged negatively, including many metallic sulfides, gold, platinum, silver, and silicic acid. It appears most probable that colloidal particles get their charge by the absorption into their mass of some simple ion already existing in the solution (most frequently the hydrogen ion  $H^+$  or the hydroxyl ion  $OH^-$ ), a little as a cork might "absorb" a tack when pressed upon it. In an electrical

field the imprisoned ion is attracted to the electrode, dragging the whole colloidal clump with it, just as the tack would be attracted by a magnet and carry the cork along with it.

**Coagulation of colloids.** When colloid particles continue to grow together into larger and larger clumps they finally form a precipitate, and this process is called *coagulation*. We have seen that a given colloid carries an electric charge due to imprisoned ions, most often  $H^+$  or  $OH^-$ . These charges, being of the same sign for a given colloid, serve to keep the clumps apart by repulsion. If we add an electrolyte to the solution, the large number of both kinds of ions introduced tends to diminish this repulsion. An imprisoned positive ion attracts some negative ion from the solution and binds it to the clump, which then becomes electrically neutral. These neutral clumps then resume the process of growing into larger clumps, and a precipitate results. In this way the introduction of an electrolyte is apt to precipitate a colloid. Bivalent ions are more efficient than univalent ones, and trivalent ones still more so. As long as the colloid remains dispersed it is often called a *hydrosol*, or a *sol*. When it has been precipitated as a gelatinous, amorphous precipitate it is called the *hydrogel*, or *gel*.

It will be evident that a hydrogel will drag down with it a certain amount of the electrolyte bound to it very intimately, and this fact is of great importance in analytical chemistry. By prolonged washing of the hydrogel, at least some of this electrolyte may often be removed, but in this case the gel shows a strong tendency to pass back into the sol condition. A colloid of this kind is said to be *reversible*. Other colloids, like colloidal metals, cannot be brought back into colloidal form when once precipitated, and these are called *irreversible*.

If we mix equivalent quantities of colloids of opposite sign, such as  $Fe_2O_3$  (positive) and  $Sb_2S_3$  (negative), a particle of the one colloid will attract a particle of the other; the two will form a neutral clump, and coagulation will result. Two colloids of the same electrical sign have no coagulating effect on each other.

**Protecting colloids.** Sometimes a colloid that is naturally unstable is made much more stable by adding some other colloid of like sign. This latter colloid is then called a *protecting* colloid. For example, in preparing colloidal gold, the red form (most finely divided) very rapidly turns purple (coarse particles). If we add a little tannic acid before we add the reducing agent, we can get a very permanent red gold colloid. The coloring matter of black ink is often a rather unstable colloidal iron gallotannate. Gum arabic, starch, or dextrin is added as a protecting colloid to prevent coagulation. In preparing photographic plates the colloidal silver salts are mixed with gelatin to render the colloidal salts stable.

**Adsorption.** The absorption of an ion by a colloid particle represents in miniature a process that goes on constantly with masses larger than colloids and which is of great importance in chemical arts and industries. Certain materials, such as charcoal, have a tendency to absorb almost incredible quantities of gases or of liquids. For this reason charcoal was used in masks in the World War to absorb poisonous gases of certain kinds from the air before it was breathed. Palladium and other metals absorb hydrogen gas. Dried silica absorbs water vapor and other gases. In fact nearly all amorphous solids absorb most gases to some extent.

There is reason to think that in many cases the absorbed gas actually forms, in real chemical union, a layer not more than 1 molecule thick all over the surface exposed. When the action is confined to the surface only, it is called *adsorption*. It is not always easy to tell whether or not the effect is limited to the surface, but *adsorption* is likely more common than *absorption*.

Adsorption depends largely upon the extent of surface presented to the gas by the solid, the larger the surface the greater being the adsorption. Evidently the adsorbing power of any solid will depend very largely on the method of its preparation, the extent of its porosity, and the fineness of its division. A cubic meter of solid divided into cubes one thousandth of a

millimeter on an edge will have a surface of about 6 square kilometers. It has been estimated that 1 g. of high-grade adsorbing charcoal has a surface of from 100 to 1000 square meters.

In some cases a capillary structure on the part of the solid seems to be necessary to create adsorption, and surface tension then comes into play. In other cases the gas seems to penetrate the solid and form a definite compound with it. Some solids suspended in liquids will adsorb dissolved materials from the liquid. Thus metallic hydroxides adsorb dyes to form lakes or to act as mordants. Fuller's earth adsorbs the yellow coloring matter from cottonseed oil in the refining of salad oil. Doubtless most catalyzers for gas reactions depend for their efficiency on their adsorbing ability, bringing the reacting gases together at high concentration in their pores, or adsorbing one component in a reversible reaction. Adsorption is therefore *selective* in character, meaning by this that some solids will adsorb certain gases or liquids but not others.

**Emulsions.** When we shake together two nearly immiscible liquids, such as an oil and water, we get a milky-looking fluid called an *emulsion*, consisting of small droplets of the one liquid (called the *internal phase*) dispersed through the continuous body of the other liquid (called the *external phase*). If the two liquids are pure, no matter how long we shake them they will soon become clear on standing, and divide into two layers, the lighter liquid floating on the heavier one.

If now we add certain substances that form colloidal dispersions, such as soap, gelatin, or albumen, and once more shake, we obtain an emulsion that is far more permanent. The added colloid is called the *emulsifying agent*. Milk is a moderately stable emulsion of water and butter-fat oil with casein as the emulsifying agent. In butter the two phases are reversed: it is an emulsion of water in butter fat. The question as to which liquid will be the external phase and which the internal phase depends largely upon the emulsifying agent employed, and not on the relative proportion of the two liquids.

Mayonnaise and many salves and ointments and soft greases, like lanolin, are typical emulsions. Most antiseptic soaps and similar preparations are emulsions of cresol (cresylic acids).

**Emulsoids.** In the chapter on States of Matter we saw that amorphous bodies are to be regarded as viscous liquids rather than as solids. Many of the metallic hydroxides, like  $\text{Fe}(\text{OH})_3$ , as well as some nonmetallic ones, like  $\text{Si}(\text{OH})_4$ , and also many salts, such as copper ferrocyanide, show little or no tendency to crystallize, but persist as amorphous bodies. On the contrary they often show a marked tendency to combine with water, and become more and more like liquids rather than like solids. In fine dispersions such bodies share to quite a degree the properties of colloids and emulsions, and are called *emulsoids* or *emulsion colloids*. In coagulating they tend to form fine films or webs rather than ordinary precipitates.

**Hydrolysis of salts.** The student may have been puzzled by an apparent contradiction in connection with the hydrolysis of salts. He has learned that most salts undergo noticeable hydrolysis in solution into free acid and base, among such salts being those of copper, iron, and aluminium. Now the hydroxides of these metals are in general insoluble, yet the solutions of their salts are clear and show no tendency to precipitate.

In the light of our knowledge of colloids the explanation of this apparent contradiction is easily found. The insoluble hydroxide or the corresponding oxide remains in the solution as a colloid and does not, as a rule, come down as a precipitate. A simple experiment will show that this is the true explanation. If to a beaker containing, say, 500 cc. of boiling water is added a few cubic centimeters of a solution of ferric chloride, the boiling solution at once develops a deep reddish-brown color, quite unlike the pale yellow of the original reagent, but identical with the color of precipitated ferric oxide. The red solution shows a strong Tyndall effect, and a single drop of concentrated sulfuric acid or solution of any sulfate (the  $\text{SO}_4$  ion) will precipitate all the iron as oxide.

**Jellies.** We have seen that an emulsion consists of droplets of one liquid dispersed through another liquid, and made stable by a protecting colloid. We have also found that emulsion colloids tend to collect into films as they coagulate. If these films inclose drops of the liquid the conditions will approach those of

an emulsion. If these drops become very numerous, the films spreading out to be very thin, and if the drops are pressed close together by the surface tension of the liquid, the drops will become distorted by the pressure of one against another. The structure of the product will now resemble a honeycomb, made up of cells with liquid content. The whole mass may have a certain elasticity and may even become quite firm. Such a product is called a *jelly* or a *gel*. Some materials such as gelatin, glue, and silicic acid form very firm jellies, and most of the oxides of the heavier metals have been prepared as jellies.

Some jellies become fluid when warmed and again "set" to a jelly when cooled. Others when once set will not again become fluid. To make a successful fruit jelly certain colloids, found abundantly in unripe fruit and called *pectins*, must be present. These act as coagulating colloids on other colloids that form the cell walls of the jelly.

If a jelly like silicic acid is slowly dried out, the cells become like capillary tubes, and such material is likely to have great adsorptive power and catalytic ability. It will be easily understood, too, why dry glue alternately adsorbs moisture and dries out again, depending upon atmospheric conditions.

It should be added that as yet we know little about the exact conditions that cause the emulsions and emulsion colloids to assume the cellular structure that leads to jelly formation.

**Smoke and fog.** The formation of smokes and fogs gives rise to many perplexing problems in chemical industry. When a dry solid burns in air to form a product that is volatile at the temperature reached in combustion, but which condenses to a solid without liquefying (like phosphorus); or when vapors are suddenly chilled below their melting points by cold air (as in distilling zinc or sulfur), the product usually forms a finely divided smoke. So, too, when dry gases combine chemically to form a solid, a smoke is usually formed, a good example being the white smoke of ammonium salts that characterizes the atmosphere of most chemical laboratories. Fogs are usually formed by supersaturated vapors coming into contact with dust particles, each solid particle serving as a point for condensation of the vapor.

The problem of condensing these smokes and fogs, either to recover a useful material or to abate a nuisance, has been a most difficult one to solve.

As a rule materials in such forms do not act chemically as we should expect them to. Thus sulfur trioxide ( $\text{SO}_3$ ) has a powerful affinity for water, uniting with it to form sulfuric acid. Yet the smoke of  $\text{SO}_3$  produced in the manufacture of sulfuric acid by the catalytic process cannot be condensed by conducting it into pure water (save by long contact). It cost a great sum of money to learn that this smoke is rapidly absorbed when it is conducted into moderately concentrated sulfuric acid.

All of these fine particles are, like colloids, electrically charged. Taking advantage of this fact, Cottrell has devised a method for settling smokes and fogs that has come into wide use. The air, laden with smoke, is passed between two plates maintained at a high difference of electrical potential. These really act as electrodes, and the charged particles are drawn to the plate of opposite sign, are discharged, and then collect into coherent dust that quickly settles. Great use is made of this process in recovering valuable materials from the stacks of smelters and from cement kilns, as well as in abating nuisances.

**The colloidal state of matter.** In an early chapter we saw that any substance might occur in the state of a solid, a liquid, or a gas. Later on we found that the condition of a dissolved substance was different from any of these, and was to be regarded as a fourth state of matter. To these four a fifth state of matter must now be added; namely, the state of colloidal dispersion. Any material may be expected to assume this state if we employ the proper manipulation to obtain it. It is important to see clearly that colloids are not to be thought of as a peculiar group of substances, but as a true state of matter.

**General applications.** The knowledge we have gained in recent years concerning the colloidal state is so extensive, and the applications of this knowledge are so numerous, that the chemistry of colloids has become a special field, and we cannot go further into it. It must suffice merely to indicate a few of the most important applications.

Most of the materials that constitute the organic structure of plants and animals are colloidal in character, and nearly all biological processes, such as those of nutrition, digestion, and secretion, depend in some way upon the properties of colloids. Soils are plastic jellies in which adsorption plays an important rôle, and

fertility depends upon colloidal processes to a very large degree. All plastic materials, such as rubber, bakelite, celluloid, plasters, cements, clays, glues, and pastes, are colloidal, and the familiar process of "setting" seems in many instances to involve jelly formation. Tanning and dyeing rest largely on adsorption and the mutual precipitation of colloids of unlike sign. The active materials of all photographic plates are colloidal, and all the films of moving pictures are also made of colloidal materials. Gums, shellacs, resins, varnishes, starches, and similar bodies are colloidal, as well as nearly all their derivatives in the arts and industries.

### QUESTIONS

1. What is a "colloidal solution"? Do you consider the term a correct one?
2. What is meant by a "colloidal precipitate"?
3. From your study of physics, do you see why the larger colloidal particles should absorb red light waves and the smaller ones the violet waves?
4. Point out the difference between electrical conduction in an ordinary electrolyte and in a colloidal dispersion.
5. What instances of adsorptive materials used for purification have we had?
6. Why is alum used in the purification of drinking water?
7. In the light of colloid chemistry, what explanation could you offer for the blue color produced by treating starch with iodine?
8. How would you classify the milky-looking sap of milkweeds?
9. What are the nine types of dispersed systems that we might have? Of how many of these can you give examples?
10. Sodium nitrate ( $\text{NaNO}_3$ ) is a very soluble salt and is extensively used as a fertilizer. Why doesn't it all wash away with the first rain?
11. Ferric hydroxide ( $\text{Fe(OH)}_3$ ) has long been used as an antidote for poisoning with arsenious acid ( $\text{H}_3\text{AsO}_3$ ). It was formerly supposed that its efficiency rested on the formation of *insoluble*  $\text{FeAsO}_3$ . Can you see any objection to this theory? (Suggestion:  $\text{Fe(OH)}_3$  is a very weak base.) Can you offer a better suggestion?
12. As a chemical act, how would you classify the hard-boiling of an egg?

## CHAPTER XXXII

### THE METALS

**Definition.** The elements which remain to be considered are collectively called *metals*, and the term at once suggests a familiar class of substances. In their chemical conduct the metals are characterized by the fact that their hydroxides, at least those of lower valence, are *bases*, and on this account they are usually referred to in chemical literature as the *base-forming elements*. When compounds of the metals are dissolved in water, ionization usually takes place in such a way that the metal becomes the cation, while the remainder of the compound acts as the anion. From this standpoint *the metals may be defined as those elements which are capable of forming simple cations when their compounds are dissolved in water.*

Neither of these definitions is entirely satisfactory. The latter depends upon the purely theoretical conception of ionization. It also classes hydrogen with the metals, although in its physical properties it has little in common with them. On the other hand, some of the metals do not have a well-defined valence lower than 3, and the hydroxide of a trivalent element is frequently amphoteric in character. The majority of the metals form more than one hydroxide, the one of higher valence usually acting as an acid; so not all the hydroxides of the metals are bases. Exclusive of organic compounds, however, it is only among the metallic elements that we find hydroxides which are always bases, and for this reason the term *base-forming element* is fairly satisfactory as a definition of a metal.

**The properties of the metals.** There are a number of properties which, in a greater or less degree, are characteristic of the metals. They reflect light brilliantly from a polished surface, or have a high *luster*. With few exceptions, notably gold and copper, they have no individually distinctive colors, but are all silvery in appearance. Most of them are *malleable*, or capable

of being hammered out into thin foil. They can also be drawn into wire, which property is designated as *ductility*. They have high *conductivity* for electricity and heat, and for the most part they have a greater *density* than the acid-forming elements.

All of these properties are greatly modified by the presence of even small percentages of impurities, as well as by the mechanical treatment to which the metal has been subjected. When cooled from the liquid state under the proper conditions, the metals are all highly crystalline, for the most part crystallizing in forms which can be referred to the isometric system of axes. In such a state they are apt to be brittle and to have little toughness, or *tenacity*. Under other conditions of preparation, especially if hammered or rolled while cooling (which process is called *annealing*), they have no very obvious crystalline form and become very much more tenacious. These facts show that it is not possible to assign exact numerical values to some of the properties of the metals. In such cases the values given are merely averages.

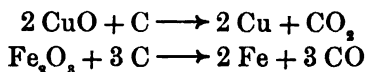
**Occurrence of the metals in nature.** A number of the metals are found in nature in the uncombined, or elementary, condition, and in this case are said to occur *native*. Among these are gold, platinum, copper, bismuth, and in general all those which stand low in the electrochemical series. As a rule the metals are found combined with acid-forming elements in the form of oxides, hydroxides, and salts of various acids. The most abundant of these salts are the silicates, carbonates, sulfides, and sulfates. All such natural substances that are essentially chemical individuals, whether they contain a metal or not, are called *minerals*. Those natural products, whether minerals or mixtures of a number of minerals, which are of value for the extraction of useful substances, or find application in their manufacture, are called *ores*.

**Extraction of metals from ores; metallurgy.** The art of extracting metals from their ores is called *metallurgy*. The metallurgy of each metal presents an individual problem

depending upon the chemical character of the metal, the nature of the ores available for its production, and its physical properties, especially its melting point. The problem is partly a physical one and partly chemical. In order to obtain the metal in the form of large masses and in a state approaching purity, it is usually necessary to prepare it at a temperature above its melting point, and draw it off from the furnace in liquid state. It is also desirable that any earthy impurity entering the furnace along with the ore should be converted into a liquid which can be easily removed. To secure this end, materials which will react with its impurities and form a liquid product are mixed with the ore. The materials so added are called *fluxes*, while the liquid produced is called *slag*. The latter usually consists of a mixture of silicates and closely resembles glass in character. The slag also acts as a liquid medium in which the small drops of melted metal can run together into larger masses, and forms a covering over the collected metal, thus protecting it from oxidation.

**Principles of metallurgy.** While the details vary in each case, there are a few definite principles employed in metallurgy which apply to the great majority of cases. Among these are the following:

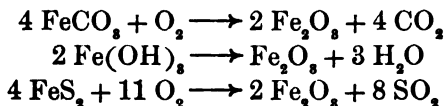
1. *Reduction of an oxide by carbon.* Many of the metals occur in nature in the form of oxides. When these are heated with carbon they are nearly all reduced, as illustrated in the equations



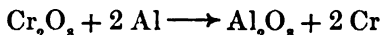
The carbon is oxidized either to the dioxide or to the monoxide, according to the temperature which it is necessary to employ.

Many ores other than the oxides can be changed into oxides by some preliminary treatment. Since some of the changes involved depend upon oxidation, the process usually consists in heating the ore with free access of air, and is called *roasting*. By this means carbonates, hydroxides, and many sulfides are

converted into oxides, as shown in the following typical equations:



2. *Reduction of an oxide by aluminium.* Not all oxides can be economically reduced by carbon, however, and in some cases in which the reduction can be effected, the metal combines with the excess of carbon to form a carbide, and so is not obtained in the pure metallic state. In such cases aluminium may sometimes be used to advantage in place of carbon. For example, the element chromium is prepared in this way:



This method has come into use as a result of the cheap production of aluminium, and is known as the *Goldschmidt method*, since it was developed by the German chemist of that name. The method may be illustrated in the following way:

**Preparation of chromium by the Goldschmidt method.** A mixture of chromium oxide and aluminium powder is placed in a Hessian crucible (*A*, Fig. 158), and on top of it is placed a small heap *B* of a mixture of sodium peroxide and aluminium, into which is stuck a piece of magnesium ribbon *C*. Powdered fluor-spar *D* is placed around the sodium peroxide, after which the crucible is set on a pan of sand and the magnesium ribbon is ignited. When the flame reaches the sodium peroxide mixture, combustion of the aluminium begins with almost explosive violence, so that great care must be taken in the experiment. The heat of this combustion starts the reaction in the chromium oxide mixture, and the oxide is reduced to metallic chromium, which collects in the bottom of the crucible.

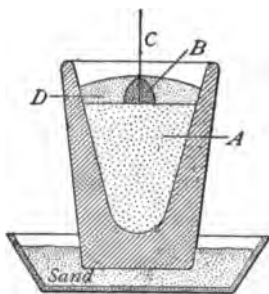
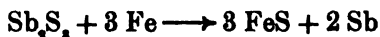


FIG. 158

3. *Reduction of sulfides by a metal.* Just as oxygen may be removed from an oxide by aluminium, so sulfur may sometimes

be removed from a sulfide by the same metal or by iron. For example, antimony and lead are sometimes desulfurized in this way :



4. *Electrical methods.* Electrical energy is employed in two very different ways in metallurgical operations. In many cases it serves merely as a source of heat, the reduction being brought about by carbon. The electric furnace has the advantage of producing a very high temperature, and is under easy control. Since the carbon serves merely as the reducing agent, and not at the same time as fuel, its quantity can be regulated to meet the requirements of the chemical reaction which it is desired to secure. A typical furnace is illustrated by the one used in the manufacture of carborundum (p. 496).

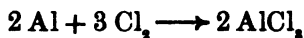
In other cases the electrical energy is employed to bring about the decomposition of a compound and the liberation of the metal without the assistance of a chemical reducing agent. Such processes are *electrolytic* in character and always take place in a liquid medium. When the metal to be produced has no action upon water, the electrolysis may be conducted in aqueous solution. The metal is then deposited directly in solid form and at ordinary temperatures, and there is no consumption of energy in maintaining the temperature. In other cases, especially those in which the metal acts upon water, some suitable compound of the metal is melted, and the resulting electrolyte is subjected to electrolysis. Almost any melted compound would serve, but many are decomposed by heat, or melt only at a temperature too high to be economical. In practical work the hydroxides or chlorides are usually employed.

Naturally the industries involving the use of large electrical currents tend to develop at localities where water power is abundant, as at Niagara Falls.

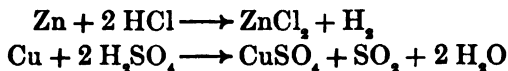
**Preparation of compounds of the metals.** A great many methods are employed in the preparation of the compounds of the metals. These compounds, which include oxides, hydroxides,

and salts, are very numerous, and each has its own peculiarities, which must be taken into account in devising means for preparing it. In many cases some rather unusual method is employed, owing to the character of the minerals available in nature or to the accumulation of a cheap by-product in some other industry. Naturally the methods employed on a small scale in the laboratory are likely to differ from those used in the industries, where economy is the first requirement. There are, however, some general principles which underlie the great majority of these methods, and it will save needless repetition to bring them into review at this point.

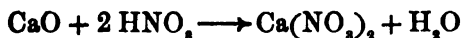
1. *Direct union of two elements.* Very many binary compounds may be prepared by heating the metal with the appropriate nonmetal. Among these are oxides, sulfides, and halides. The product in such cases is, of course, anhydrous, and this method finds wide application when it is the *anhydrous* rather than the *hydrated* compound that is wanted. The method is most frequently employed in the preparation of anhydrous halides, as, for example, aluminium chloride:



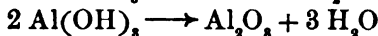
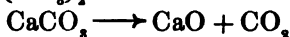
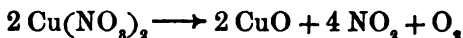
2. *Treatment of a metal, or its oxide or hydroxide, with an acid.* Since most of the metals are produced commercially in a high degree of purity, the metals themselves are often the most convenient starting point for the preparation of their compounds on a small scale in the laboratory. For example, the salts of zinc and copper are frequently made in this way:



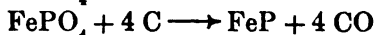
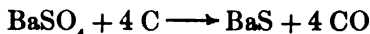
In the industries the hydroxide or oxide is more likely to be employed, since it is usually found in nature or is of easy preparation. For example, calcium salts are often prepared from lime ( $\text{CaO}$ ), as in the case of the nitrate:



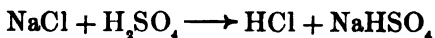
3. *Decomposition of compounds.* The decomposition of compounds, either by heat alone or in connection with a reducing agent, frequently leads to the formation of simpler ones. For example, nitrates, carbonates, and hydroxides, when heated sufficiently, usually yield oxides:



When heated with carbon the various salts of oxygen acids are usually reduced and yield a binary compound of the metal with the acid-forming element. For example, sulfates yield sulfides and phosphates yield phosphides, as shown in the equations



4. *Displacement of a volatile acid.* When a nonvolatile acid acts upon a salt of a volatile acid, the latter is displaced in accordance with the general principles of equilibrium, *provided the volatile acid is sparingly soluble* in any liquid which may be present. For example, the reaction of sulfuric acid with sodium chloride goes on to conclusion if the sulfuric acid employed is quite concentrated, for hydrogen chloride is very sparingly soluble in this liquid:

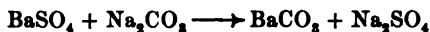


In dilute solution the reaction results in an equilibrium, for in this case the hydrogen chloride is freely soluble in the solution.

5. *Methods based upon precipitation.* The formation of a precipitate when two electrolytes are brought together in solution takes place in accordance with the principles of ionic equilibrium developed in Chapter XVIII. *In general it may be said that when two salts, or a strong acid and a salt, are brought together in solution, double decomposition takes place, with the formation of a precipitate if the union of any pair of ions produces an insoluble salt.* When a salt is treated with a *weak acid*, however, no precipitate is formed, even though double decomposition

would result in the formation of an insoluble salt, unless the latter is extremely insoluble. It can also be shown that the *salts of strong acids*, such as sulfates or chlorides, when insoluble in water are also insoluble in dilute acids. *Salts of weak acids*, such as carbonates, sulfites, and sulfides, though insoluble in water, are soluble in dilute acids. These principles are of constant application in the preparation of compounds.

6. *Fusion methods.* When compounds are melted together, it sometimes happens that double decomposition occurs, which would not take place if the same salts were brought together in water. In such fusion reactions one of the melted salts may be regarded as the solvent, and it is to be expected that the solubility of the other in this will be different from its solubility in water. For example, barium sulfate is practically insoluble in water, and consequently it is not greatly affected by aqueous solutions of sodium carbonate. In melted sodium carbonate, on the contrary, it is readily soluble, while barium carbonate is insoluble. As a consequence, when it is melted together with sodium carbonate, the following double decomposition takes place:



When the mixture is cooled and warmed with water, all the compounds except barium carbonate dissolve, and this may then be filtered off and converted into any desired salt. This forms a convenient method of passing from an insoluble salt of a strong acid to a similar salt of a weak acid. It will be recalled that natural silicates can be decomposed in the same way.

**The theory of precipitation.** It is a very easy matter to learn a few simple rules governing precipitation, such as those given in method 5, but it is very much more important to understand why these rules hold good. This is not difficult if it is kept steadily in mind that *all salts ionize freely in solution*, but that *acids differ among themselves very greatly* as to their degree of ionization. Strong acids are about as much ionized as are salts, while *very weak acids may be ionized not much more than water itself*. With these facts in view, three general cases present themselves for consideration.

1. *Double decomposition between two salts.* When two salts, such as  $\text{CuSO}_4$  and  $\text{BaCl}_2$ , are brought together in solution we have an abundance of all four ions  $\text{Cu}^{++}$ ,  $\text{SO}_4^{--}$ ,  $\text{Ba}^{++}$ , and  $\text{Cl}^-$ , and these are all free to form any possible combination. So we shall soon have not only molecules of the two original salts, but also of the two new combinations  $\text{BaSO}_4$  and  $\text{CuCl}_2$ , and each of these will be in equilibrium with the pair of ions producing it.

In the case of  $\text{BaSO}_4$  the equilibrium will be  $\text{BaSO}_4 \rightleftharpoons \text{Ba}^{++}, \text{SO}_4^{--}$ , and in a solution of ordinary concentration we should expect about half the salt to be molecules and half ions. The concentration equation will be

$$\frac{[\text{Con. Ba}^{++}] \times [\text{Con. SO}_4^{--}]}{[\text{Con. BaSO}_4]} = k$$

in which  $k$  (the equilibrium constant) will be a number not far from 0.5. For the present purpose it is more convenient to write this equation in the form

$$[\text{Con. Ba}^{++}] \times [\text{Con. SO}_4^{--}] = k [\text{Con. BaSO}_4] \quad (1)$$

*Solubility product.* It should be clear from equation (1) that the more  $\text{Ba}^{++}$  and  $\text{SO}_4^{--}$  ions brought into the solution, the more  $\text{BaSO}_4$  will be formed at equilibrium. But the solubility of *any* salt is limited, and when saturation is reached *the excess will be precipitated*. When this condition of saturation is reached, the concentration of the  $\text{BaSO}_4$  becomes unchangeable, no matter how much  $\text{Ba}^{++}$  and  $\text{SO}_4^{--}$  we may add, for all beyond this constant saturation quantity will be thrown out of solution.

This unchangeable concentration of the molecules of  $\text{BaSO}_4$  at saturation, may be designated by a constant  $k'$  (the solubility constant). At saturation, equation (1) will then become

$$[\text{Con. Ba}^{++}] \times [\text{Con. SO}_4^{--}] = k k' = K \quad (2)$$

*The constant  $K$  is called the solubility product.* It is equal to the product of the concentrations of the two ions at saturation, and it should be noticed that these two concentrations are in general *not equal* to each other, since the two ions came from different salts brought together in accidental ratio.

The solubility product  $K$  is also numerically equal to the product of two other constants: the one is the equilibrium constant, in general equal to a number somewhere near 0.5; the other constant is the solubility of the salt expressed in gram-molecules per liter, and this may have a wide range of values. In the salts we think of as "insoluble" it is *very small*. Barium sulfate dissolves to the extent of 2.3 mg. per liter which is a gram-molecular concentration of 0.00001. Consequently, we have the solubility product of  $\text{BaSO}_4$  as follows:

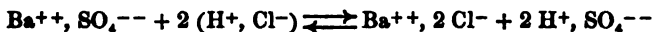
$$[\text{Con. Ba}^{++}] \times [\text{Con. SO}_4^{--}] = K = 0.5 \times 0.00001 = 0.000005$$

Whenever the two ions  $\text{Ba}^{++}$  and  $\text{SO}_4^{--}$  are brought together in solution they will precipitate as insoluble  $\text{BaSO}_4$  until the product of the concentration of the two ions remaining in solution comes down to this value. Since all salts have at least *some* solubility, precipitation will never be entirely complete.

2. *Double decomposition between a salt and a strong acid.* If we bring together a salt and a *strong acid*, for example  $\text{BaCl}_2$  and  $\text{H}_2\text{SO}_4$ , the conditions of equilibrium are practically the same as in the case of two salts, for both compounds are freely ionized, and all the ions are free to set up new equilibria. Precipitation of  $\text{BaSO}_4$  will occur until the concentrations of the  $\text{Ba}^{++}$  ion and the  $\text{SO}_4^{--}$  ion are cut down to satisfy the solubility product

$$[\text{Con. Ba}^{++}] \times [\text{Con. SO}_4^{--}] = K$$

On the other hand, the insoluble precipitate *will not dissolve in even a strong acid*, such as  $\text{HCl}$ . For, if it were to dissolve according to the equation



the concentration of  $\text{Ba}^{++}$  and  $\text{SO}_4^{--}$  would almost at once reach values such that

$$[\text{Con. Ba}^{++}] \times [\text{Con. SO}_4^{--}] > K$$

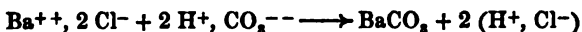
and precipitation would occur. *The insoluble salt of a strong acid is insoluble in acids as well as in water.*

3. *Double decomposition between a salt and a weak acid.* If we bring together a salt and a *weak acid* the conditions are notably different from those of the two former cases. The salt will ionize freely, *but the acid will supply few ions.* For example,  $\text{BaCO}_3$  has about the same solubility as has  $\text{BaSO}_4$ , and the solubility product is therefore about the same for the two salts.

$$[\text{Con. Ba}^{++}] \times [\text{Con. CO}_3^{--}] = K \text{ (a very small constant)}$$

When we bring together  $\text{BaCl}_2$  and  $\text{H}_2\text{CO}_3$ , however, we obtain no precipitate, the reason being that  $\text{H}_2\text{CO}_3$  furnishes very few  $\text{CO}_3^{--}$  ions; and although  $\text{Con. Ba}^{++}$  may be rather large,  $\text{Con. CO}_3^{--}$  is so small that the *product* of the two never exceeds the solubility product  $K$ .

The reaction does go on to a slight extent, forming  $\text{BaCO}_3$  in solution, according to the equation



But the  $\text{HCl}$  produced is *freely ionized*, and the  $\text{H}^+$  ions from this source at once diminish still further the small ionization of  $\text{H}_2\text{CO}_3$ , as may be seen from the equilibrium equation:

$$\frac{[\text{H}^+] \times [\text{H}^+] \times [\text{CO}_3^{--}]}{[\text{H}_2\text{CO}_3]} = k \text{ (very small)}$$

Any  $\text{H}^+$  added from another source (as from  $\text{H}^+, \text{Cl}^-$ ) will increase the  $\text{H}^+$  in the numerator of the equation, causing  $\text{H}^+$  to combine with  $\text{CO}_3^{--}$  to restore equilibrium and so diminish the concentration of  $\text{CO}_3^{--}$ .

On the other hand, if we expose the insoluble  $\text{BaCO}_3$  to the action of a strong acid, such as  $\text{H}^+$ ,  $\text{Cl}^-$ , it will dissolve. For, as fast as the salt forms a saturated solution according to the solubility equation

$$[\text{Con. Ba}^{++}] \times [\text{Con. CO}_3^{--}] = K$$

the  $\text{H}^+$  ions of the added acid at once combine with the  $\text{CO}_3^{--}$  ions supplied by the solubility equilibrium to form *un-ionized*  $\text{H}_2\text{CO}_3$ . More  $\text{BaCO}_3$  then passes into solution and the process continues until all of the salt has dissolved. *The insoluble salt of a weak acid will dissolve in a strong acid.*

4. *Precipitation in case of extremely insoluble compounds.* From the explanation that has just been given, it will be seen that if a given salt has an *extremely small solubility*, then even a weak acid may precipitate it. For example, most of the sulfides of the metals are "insoluble" in water, but some are very much more insoluble than others. Consequently the weak acid  $\text{H}_2\text{S}$  will precipitate the most insoluble ones even in the presence of a strong acid, but it is too little ionized to precipitate the more soluble ones even in neutral solution. Many of the reactions employed in analytical chemistry depend on just these slight differences in solubility on the part of "insoluble" salts.

**Insoluble compounds.** From the foregoing discussion it will at once be evident that a knowledge of the solubility of compounds is an important part of a training in chemistry. With this knowledge it is possible, in many cases, to predict the course of a reaction and to devise ways in which to prepare desired compounds. For precise information a dictionary of solubilities must be consulted, but it is possible to make a few general statements, which will be of assistance in understanding the reactions of the following chapters. These statements apply only to normal salts and do not include the salts of rare elements. Acid salts are apt to be more soluble than normal salts, and basic salts less so.

1. **Hydroxides.** All hydroxides are insoluble in water except those of ammonium, sodium, potassium, calcium, strontium, and barium.

2. **Nitrates.** All nitrates are soluble in water.

3. **Chlorides.** All chlorides are soluble in water except silver and mercurous chlorides. (Lead chloride is slightly soluble.)

4. **Sulfates.** All sulfates are soluble in water except those of barium, strontium, and lead. (Sulfates of silver and calcium are only moderately soluble.)

5. *Sulfides*. All sulfides are insoluble in water except those of ammonium, sodium, and potassium. The sulfides of calcium, strontium, barium, and magnesium are insoluble in water, but are changed by hydrolysis into acid sulfides which are soluble. On this account they cannot be prepared by precipitation.

6. *Carbonates, sulfites, phosphates, and silicates*. All of these normal salts are insoluble in water except those of ammonium, sodium, and potassium.

**Comments on equations.** In the succeeding chapters the methods used in preparing many different salts are described very briefly. In the majority of cases the reactions are ionic in nature and involve the precipitation of a relatively insoluble compound, or the formation of a sparingly ionized compound, or an insoluble gas. In simple reactions of double decomposition it will not be necessary to write the equations in ionic form. When the application of the ionic theory is not so apparent, the equations will indicate the ions taking part in the reactions.

### QUESTIONS

1. In the reduction of an oxide with carbon, what will determine whether  $\text{CO}$  or  $\text{CO}_2$  will be formed?

2. Why should aluminium be an effective reducing agent? Would calcium or magnesium serve equally well?

3. Could a sulfate be reduced to metal by carbon? What would the reduction product be?

4. What metals could be produced by the electrolysis of aqueous solutions of their salts?

5. Which would be easier to reduce, a sulfate or a phosphate? Why?

6. Suggest two ways of preparing anhydrous aluminium sulfide ( $\text{Al}_2\text{S}_3$ ).

7. Write the equation for the reaction that occurs when calcium silicate,  $\text{CaSiO}_3$ , is fused with sodium carbonate,  $\text{Na}_2\text{CO}_3$ .

8. Some sulfates, chlorides, carbonates, sulfides, sulfites, and phosphates are insoluble. Which of these classes should be soluble in nitric acid (excluding all reactions of oxidation)?

9. Suggest a method for preparing each of the following compounds: (a) magnesium sulfate ( $\text{MgSO}_4$ ); (b) copper nitrate ( $\text{Cu}(\text{NO}_3)_2$ ); (c) ferrous sulfide ( $\text{FeS}$ ); (d) zinc chloride ( $\text{ZnCl}_2$ ).

10. In general which compounds of a metal serve best for the preparation of the other compounds of the metal?

### PROBLEMS

1. Barium sulfate is soluble to the extent of 2.3 mg. per liter at ordinary temperatures. Express this solubility in terms of gram-molecular concentration.

2. The solubility of calcium sulfate at  $20^\circ$  is 2.042 g. per liter, and the saturated solution is ionized to the extent of 52.4 per cent.

(a) Express the concentration in terms of gram-molecules per liter.

(b) Calculate the gram-molecular concentration of each of the ions and of the un-ionized salt.

(c) Calculate the value of the solubility product.

(d) Calculate the value of the equilibrium constant.

## CHAPTER XXXIII

### THE ALKALI METALS

METAL	ATOMIC WEIGHT	DENSITY	MELTING POINT	BOILING POINT	FIRST PREPARED
Lithium (Li) . . . .	6.94	0.584	186.0°	1400°+	Arfvedson, 1817
Sodium (Na) . . . .	23.00	0.971	97.5°	877°	Davy, 1807
Potassium (K) . . .	39.10	0.862	62.3°	758°	Davy, 1807
Rubidium (Rb) . . .	85.45	1.532	38.0°	696°	Bunsen, 1861
Cæsium (Cs) . . . .	132.81	1.870	28.0°	670°	Bunsen, 1860

**Characteristics of the family.** The elements listed in the above table constitute a family in Group I of the periodic table. They are called the alkali metals for the reason that the most familiar members of the family, namely, sodium and potassium, are constituents of compounds that have long been known as alkalies.

The alkali metals, as shown in the above table, are light metals of low melting point. They are very soft and when pure have a bright metallic luster. Their position at the head of the electrochemical series designates them as very active metals: hence they do not occur free in nature. They are univalent, and, with very few exceptions, their compounds are white solids, soluble in water.

Sodium and potassium are by far the most important members of the family.

#### LITHIUM

**The element.** Lithium was discovered in 1817 by Arfvedson, a student of Berzelius, although he did not succeed in isolating the metal itself. This was first accomplished by Bunsen in 1855. Its compounds are widely but sparingly distributed, being found in many mineral waters and in nearly all igneous

rocks, from which it finds its way into the soil. Certain plants, such as the sugar beet and tobacco, absorb small quantities of lithium compounds from the soil, and when such plants are burned, the lithium remains in the ash in the form of the carbonate. Some of the most important of the lithium minerals are lepidolite, found in California, and spodumene and amblygonite, found in South Dakota. These are complex compounds and contain from 4 to 10 per cent of lithium. They are being used in the manufacture of opal glass and enamels.

Lithium may be prepared by the electrolysis of its fused chloride or of a solution of the chloride in some solvent, such as pyridine, which is not acted upon by the metal. It is the lightest of all the elements that are solid at ordinary temperature, having a density of only 0.534. It has a strong affinity for nitrogen and unites with it even at ordinary temperatures. The metal is expensive and has no commercial uses.

**Compounds of lithium.** The element forms many compounds, but only a very few are of any commercial importance. When heated in a Bunsen flame, most of these compounds volatilize and impart to the flame a crimson color. Even when the quantity present is so small that the flame is not visibly colored, the presence of the element may be recognized by viewing the flame through the spectroscope. Lithium compounds are prepared by dissolving lithium minerals in acids and precipitating lithium from the solution in the form of the carbonate. This can be changed into other salts by the action of the appropriate acid. Some of the most important of the lithium compounds are the following:

*Lithium chloride* ( $\text{LiCl}$ ) is prepared directly from the lithium minerals and, like the carbonate, is used in the preparation of other lithium compounds. *Lithium bromide* ( $\text{LiBr}$ ) is used in medicine. *Lithium carbonate* ( $\text{Li}_2\text{CO}_3$ ) is also used in medicine. It is but slightly soluble in water and is one of the few compounds whose solubility decreases with rise in temperature—100 g. of water at  $20^\circ$  dissolving 1.33 g. of the carbonate and

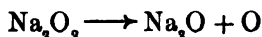
at 100°, 0.73 g. *Lithium phosphate* ( $\text{Li}_3\text{PO}_4$ ), like the carbonate, is but slightly soluble in water. The sparing solubility of the carbonate and phosphate is noteworthy, since, with these exceptions, all the common compounds of the alkali metals are readily soluble.

### THE COMPOUNDS OF SODIUM

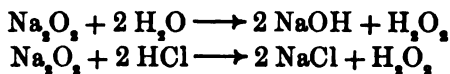
**NOTE.** The metal sodium, as well as its hydroxide, was discussed in Chapter XIV. It is desirable for the student to review this discussion in connection with the study of the other members of the family.

**General.** In addition to sodium hydroxide (p. 214) sodium forms a large number of compounds. With the exception of the nitrate all these compounds are prepared from the chloride, since it is so abundant and inexpensive. The processes involved are often complicated, owing to the fact that the compounds of sodium are all soluble and therefore cannot be prepared directly from the chloride by precipitation; moreover, the chloride is a salt of a strong acid and is not readily acted upon by most other acids. Experiments have shown that the most economical method of procedure consists either in first changing the chloride into the hydroxide by the electrolysis of its aqueous solution or in converting it into the carbonate by the methods to be described. Since the hydroxide is a base and the carbonate is a salt of a very weak volatile acid, both are readily changed into other compounds.

**The oxides of sodium.** The metal forms two oxides, namely, sodium oxide ( $\text{Na}_2\text{O}$ ) and sodium peroxide ( $\text{Na}_2\text{O}_2$ ). The former is obtained, mixed with the peroxide, when sodium is burned in a limited supply of air. The peroxide is more easily obtained pure, and is of much the greater importance, since it serves as an excellent oxidizing agent. It is a yellowish-white powder prepared by passing air, freed from moisture and carbon dioxide, through an iron tube containing sodium heated to about 300°. While the pure compound is stable toward heat, in the presence of an oxidizable substance it gives up half of its oxygen:



It is readily acted upon by water and acids:



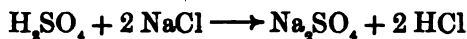
The hydrogen peroxide formed in the reactions decomposes into water and oxygen unless the temperature is kept low. It will be recalled that the reaction with water serves as one of the methods given for preparing oxygen.

**Sodium chloride (common salt) (NaCl).** Sodium chloride is very widely distributed in nature. Thick strata, evidently deposited by the evaporation of salt water, are found in many places. In the United States the most important localities for salt are New York, Michigan, Ohio, and Kansas. Sometimes the salt is mined, especially if it is in the pure form called *rock salt*. Very frequently a strong brine is pumped from deep wells sunk into the salt deposit, and is then evaporated in large pans until the salt crystallizes out. The crystals are in the form of small cubes and contain no water of crystallization. Salt melts at 801° and above this temperature begins to volatilize.

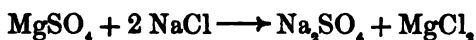
Salt is used in the preparation of nearly all substances containing either sodium or chlorine. These include many products of the highest importance to civilization, such as soap, glass, hydrochloric acid, soda, and bleaching powder. To meet these demands over 7,000,000 tons of salt are produced annually in the United States. Small quantities are essential to animal life. Pure salt does not absorb moisture, though we usually think it does; the fact that ordinary salt becomes moist in air is due to the presence of certain deliquescent compounds, especially the chlorides of calcium and magnesium.

**Sodium bromide (NaBr); sodium iodide (NaI).** These compounds somewhat closely resemble sodium chloride in their physical properties. They can be prepared by the action of bromine and iodine respectively upon a solution of sodium hydroxide, the reaction being similar to that of chlorine upon bases (p. 373). They are used to a limited extent in photography.

**Sodium sulfate ( $\text{Na}_2\text{SO}_4$ ).** Large quantities of this compound are prepared for use in the manufacture of glass and sodium carbonate. It is obtained by the action of sulfuric acid upon sodium chloride:



It will be recalled that this reaction serves as the principal source of hydrochloric acid (p. 200). Sodium sulfate is also prepared by the action of sodium chloride upon magnesium sulfate, the latter being obtained in large quantities as a by-product in the manufacture of potassium chloride:

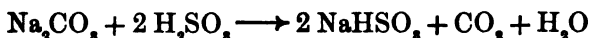


Sodium sulfate is the least soluble of the compounds represented in the equation, and separates when hot saturated solutions of magnesium sulfate and sodium chloride are mixed.

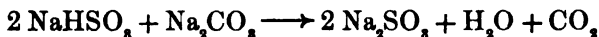
Under ordinary conditions sodium sulfate crystallizes from water in the form of a decahydrate ( $\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$ ). This is known as *Glauber's salt*, from the alchemist Glauber, who lived about the middle of the seventeenth century, and who first used the compound in medicine. Considerable deposits of this hydrate are found in nature. The transition point between the decahydrate and the anhydrous salt is  $32.384^\circ$  (p. 184), and this point is so definite that it has been suggested by Richards and Wells as a suitable fixed temperature for use in the calibration of thermometers.

By the action of sulfuric acid, sodium sulfate is converted into the acid sulfate  $\text{NaHSO}_4$ , commonly known as sodium bisulfate.

**Sulfites of sodium.** The acid sulfite  $\text{NaHSO}_3$ , often called sodium bisulfite, is formed by saturating a solution of sodium carbonate with sulfur dioxide. Sulfurous acid is first formed by the union of the dioxide with water, and this decomposes the carbonate:



The normal sulfite  $\text{Na}_2\text{SO}_3$  is prepared by adding sodium carbonate to a saturated solution of the acid sulfite in the proportion indicated in the following equation:

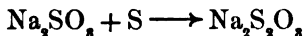


These two reactions depend upon the extremely small ionization of carbonic acid and its ready decomposition into water and insoluble carbon dioxide:

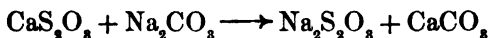


Both of the sulfites readily absorb oxygen, forming the corresponding sulfates; they are therefore reducing agents. They are used to some extent as bleaching agents and as preservatives.

**Sodium thiosulfate ( $\text{Na}_2\text{S}_2\text{O}_3$ ).** This salt is made by adding sulfur to a solution of sodium sulfite and warming the mixture:

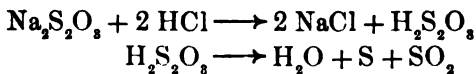


Upon evaporation the resulting solution yields the pentahydrate  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5 \text{H}_2\text{O}$ , which is commonly known as *hyposulfite of soda*, or simply *hypo*. It is also prepared from the calcium sulfide obtained as a by-product in the manufacture of sodium carbonate. Upon exposure to air the calcium sulfide is oxidized to calcium thiosulfate, which is then treated with sodium carbonate:

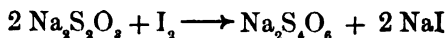


The insoluble calcium carbonate is filtered off, and the sodium thiosulfate is obtained by evaporating the filtrate.

Sodium thiosulfate is very soluble in water, in which it readily forms supersaturated solutions. Acids react with it, liberating free sulfur, for thiosulfuric acid is very weak and unstable:



Dilute solutions exposed to the air undergo a similar change due to the action of carbonic acid. The salt reacts with free iodine, forming sodium iodide and sodium tetrathionate:

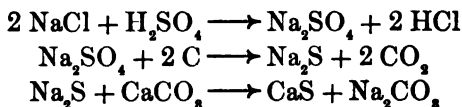


This reaction is used for determining the quantity of free iodine present in a solution. The liquid is first colored blue by the addition of a few drops of starch solution (p. 365). A solution of sodium thiosulfate of known strength is then slowly run in from a burette until the blue color just disappears, thus indicating that all the iodine has entered into combination. From the amount of sodium thiosulfate added one can easily calculate the quantity of iodine present.

The salt is used very largely in photography as a solvent for silver salts (see photography) and as an "antichlor" for removing any chlorine remaining in substances bleached with this element.

**Sodium carbonate (soda ash) ( $\text{Na}_2\text{CO}_3$ ).** This very important compound occurs in nature to a limited extent in certain arid regions. Many seaweeds are rich in sodium compounds absorbed from the water. When these are burned, sodium carbonate remains in the ashes, which suggested the name *soda ash*. At present it is all made from sodium chloride by two general methods.

1. **Leblanc process.** This older process, named after the French chemist who devised it, is no longer used in the United States but is still used in Europe. It involves several distinct reactions, the most important ones being represented in the following equations:

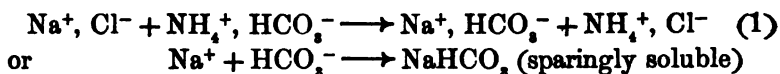


In a manufacturing plant the last two reactions take place in one process. Sodium sulfate, coal, and powdered limestone are heated together to a rather high temperature. The coal reduces the sulfate to sulfide, which fuses and reacts upon the calcium carbonate. Some limestone is decomposed by the heat, forming calcium oxide. When treated with water the calcium oxide is changed into hydroxide, and this prevents the insoluble calcium sulfide from being rapidly hydrolyzed into the soluble calcium acid sulfide  $\text{Ca}(\text{HS})_2$ , which would react with the sodium carbonate to form the insoluble calcium carbonate.

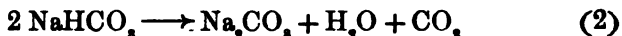
The crude product of the process is a hard black cake called *black ash*. When this mass is digested with water, the sodium carbonate passes into solution. The pure carbonate is obtained by the evaporation of this solution, crystallizing from it in crystals of the formula  $\text{Na}_2\text{CO}_3 \cdot 10 \text{H}_2\text{O}$ . Since over 60 per cent of this salt is water of hydration, the crystals are usually heated until it is driven off. The product is called calcined soda, or *soda ash*.

2. *Solvay process.* This more modern process is also named after its discoverer, who is a distinguished Belgian chemist and one of the very few foreign honorary members of the American Chemical Society. The process depends upon two consecutive reactions.

When concentrated solutions of sodium chloride and of ammonium hydrogen carbonate are brought together, the solubility product of the sparingly soluble sodium hydrogen carbonate is exceeded and the excess of the salt is precipitated, as represented in equation (1):



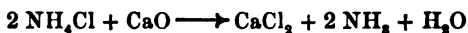
This is converted into the normal carbonate by heating, the reaction being represented in the equation



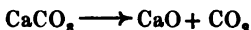
In the Solvay process a very concentrated solution of salt is first saturated with ammonia gas, and a current of carbon dioxide is then conducted into the solution. In this way ammonium hydrogen carbonate is formed:



This enters into double decomposition with the salt, as shown in equation (1) under the Solvay process. After the sodium hydrogen carbonate has been precipitated the mother liquors containing ammonium chloride are treated with lime:



The lime is obtained by burning limestone:



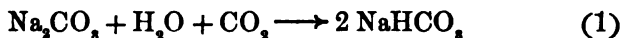
The ammonia and carbon dioxide evolved in these reactions are used in the preparation of an additional quantity of ammonium hydrogen carbonate. There is, therefore, no loss of ammonia; the only materials permanently used up are salt and lime, while the only by-product is calcium chloride.

**Historical.** In former times sodium carbonate was obtained principally from the ashes of certain plants. During the French Revolution this supply was cut off, and in behalf of the French government Leblanc made a study of methods of preparing the carbonate directly from salt. As a result he devised the method which bears his name, and which was used exclusively for many years. It has been replaced to a large extent by the Solvay process, which has the advantage that salt and lime are inexpensive, and that the

ammonium hydrogen carbonate used can be regenerated from the products formed in the process. Much expense is also saved in fuel, and the sodium hydrogen carbonate, which is the first product of the process, has itself many commercial uses.

**Properties and uses of sodium carbonate.** The aqueous solution of the salt is basic in character (p. 327). With water the salt forms a number of different hydrates, the most common of which is the decahydrate  $\text{Na}_2\text{CO}_3 \cdot 10 \text{H}_2\text{O}$ . By cooling a hot solution of the salt this hydrate is obtained in the form of large, clear, monoclinic crystals and is often known as *washing soda*, or *sal soda*. It effloresces on exposure to dry air, changing into the monohydrate. The transition point of the decahydrate into the heptahydrate  $\text{Na}_2\text{CO}_3 \cdot 7 \text{H}_2\text{O}$  is  $32^\circ$ , and of this into the monohydrate,  $35.37^\circ$ . The anhydrous salt melts at  $853^\circ$  and along with potassium carbonate is used for decomposing silicates (p. 495). Mere mention of the fact that sodium carbonate is used in the manufacture of glass, soap, and many chemical reagents will indicate its importance in the industries. Enormous quantities of it are manufactured for these various uses.

**Sodium hydrogen carbonate (bicarbonate of soda, baking soda) ( $\text{NaHCO}_3$ ).** This salt is prepared either by the Solvay process, as already explained, or by passing carbon dioxide into saturated solutions of sodium carbonate:



The bicarbonate, being but sparingly soluble, precipitates. When the solid is heated the reaction is reversed, and the bicarbonate changes into the carbonate with liberation of carbon dioxide. The salt is used as an aërating agent in baking. For this purpose it must be mixed with some substance, such as sour milk or cream of tartar (p. 453), which slowly reacts with the carbonate, liberating carbon dioxide.

**Commercial production of carbon dioxide.** Advantage is taken of the reaction expressed in equation (1) above for the purification of carbon dioxide on a large scale for use in the preparation of carbonated beverages. Coal is burned under a steam boiler, and the resulting carbon dioxide is conducted

into large towers filled with coke over which trickles a concentrated solution of sodium carbonate. The carbon dioxide is absorbed, forming sodium bicarbonate. The product is then heated by the steam generated in the boiler, forming carbon dioxide, which is collected, and sodium carbonate, which is used over again. The process thus becomes continuous.

**Cream of tartar baking powders.** Cream of tartar baking powders consist of a mixture of cream of tartar, bicarbonate of soda, and some starch or flour. When water is added to this mixture, the cream of tartar slowly acts upon the soda, liberating carbon dioxide in accordance with the following equation:  $\text{KHC}_4\text{H}_4\text{O}_6 + \text{NaHCO}_3 \longrightarrow \text{KNaC}_4\text{H}_4\text{O}_6 + \text{H}_2\text{O} + \text{CO}_2$

The carbon dioxide escapes through the dough, making it light and porous. The starch is added to absorb any moisture present in the other ingredients of the powder, and thus to prevent their interaction until the powder is used.

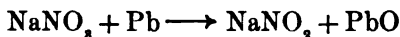
**Phosphate baking powders.** Some baking powders contain primary calcium or sodium phosphate in place of cream of tartar:



**Sodium nitrate (Chile saltpeter) ( $\text{NaNO}_3$ ).** This substance is found in certain arid regions, where it has apparently been formed by the decay of organic substances in the presence of air and sodium salts. The largest deposits are in Chile, and most of the nitrate of commerce comes from that country. Smaller deposits occur in California and Texas. The crude nitrate is known as *caliche*. The commercial salt is prepared by treating the caliche with water, allowing the insoluble earthy materials to settle, and evaporating to crystallization the clear solution so obtained. The soluble impurities remain for the most part in the mother liquors.

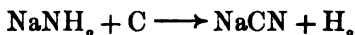
Since this salt is the only nitrate found extensively in nature, it is the material from which other nitrates, as well as nitric acid, are prepared. It is used in enormous quantities in the manufacture of sulfuric acid and potassium nitrate, and as a fertilizer.

**Sodium nitrite ( $\text{NaNO}_2$ ).** When sodium nitrate is heated with lead, sodium nitrite is formed:



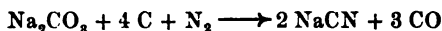
It is largely used in the preparation of certain compounds of carbon, especially dyes.

**Sodium cyanide (NaCN).** This salt of hydrocyanic acid is prepared from sodium. The sodium is first changed into sodamide (p. 255). The resulting sodamide is then converted into sodium cyanide by heating with carbon:



An increasing amount of the salt is also being made by heating a mixture of calcium cyanamide and carbon (p. 565) with sodium chloride. The aqueous solution of the salt is alkaline. The salt readily dissolves gold and is used for extracting this metal when it is scattered in small quantities through earthy material. It is also used in electroplating baths as well as in the manufacture of hydrocyanic acid (p. 386). Like the acid, it is extremely poisonous.

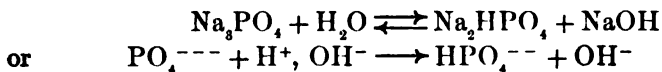
**Bucher process for making sodium cyanide.** The American chemist Bucher has devised a process for making sodium cyanide by passing nitrogen through tubes containing a mixture of sodium carbonate, coke, and finely divided iron, the latter acting as a catalyzer. If the temperature is maintained at about 1000°, a reaction takes place resulting in the formation of sodium cyanide:



During the World War the government erected at Saltville, Va., a plant designed to produce by this process 10 tons of sodium cyanide daily. The plant was completed, but was operated only on a limited scale when the armistice was signed. At its present stage of development, the process can hardly compete with the sodium process for the manufacture of cyanides.

**Sodium phosphates.** Since phosphorus forms a number of acids, most of which are polybasic, one can readily understand why so many different phosphates of sodium are known. The names and formulas of the sodium salts of orthophosphoric acid have already been given (p. 468), and only these compounds will be discussed.

1. **Normal sodium phosphate ( $\text{Na}_3\text{PO}_4$ ).** Although this is a normal salt, its aqueous solution has a strong basic reaction, due to partial hydrolysis:



It is prepared by adding sodium hydroxide to a solution of disodium phosphate and evaporating to crystallization. The excess of sodium hydroxide reverses the reaction of hydrolysis, and the normal salt separates in the form of crystals having the formula  $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ . The salt is sometimes used in laundries for softening water. It not only precipitates the calcium and magnesium salts present, but at the same time leaves the water slightly basic in reaction.

2. *Disodium phosphate* ( $\text{Na}_2\text{HPO}_4$ ). This is the most common of the phosphates of sodium and is generally known simply as sodium phosphate. It occurs in blood and urine, and it was from these sources that the salt was first obtained. It is prepared by the action of phosphoric acid upon sodium carbonate:



The salt crystallizes from solution in the form of the hydrate  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ . This is the salt commonly used when a soluble phosphate is needed.

3. *Monosodium phosphate* ( $\text{NaH}_2\text{PO}_4$ ). This salt is prepared by the action of phosphoric acid upon disodium phosphate:



**Other compounds of sodium.** Sodium forms both the acid and normal salts of hydrosulfuric acid, namely,  $\text{NaHS}$  and  $\text{Na}_2\text{S}$ . The former is made by saturating a solution of sodium hydroxide with hydrogen sulfide and the latter by reducing sodium sulfate with carbon. *Sodium pyroantimonate* ( $\text{Na}_2\text{H}_2\text{Sb}_2\text{O}_7 \cdot 6\text{H}_2\text{O}$ ) is the least soluble of all the compounds of sodium. *Sodium chlorate* ( $\text{NaClO}_3$ ) is often used as an oxidizing agent as well as in the preparation of oxygen in the laboratory.

## POTASSIUM

**Occurrence.** Potassium is a rather abundant element, being a constituent of many igneous rocks, especially the feldspars and micas. Sea water, as well as most mineral waters, contains small percentages of its compounds. Very large deposits of the chloride and sulfate, associated with compounds of calcium and

magnesium, occur in the region of Stassfurt, Germany, and are known as *Stassfurt salts*. Similar deposits consisting chiefly of the chloride (sylvite) occur in southern Alsace, France. It is also found in small quantities as the nitrate (saltpeter) and in many other forms.

The natural decomposition of rocks containing potassium gives rise to various compounds of the element in all fertile soils. It is absorbed by growing plants and is a characteristic constituent of land plants, just as sodium is of sea plants. Some of the sea plants, however, as, for example, the giant algae of the California coast, contain potassium chloride amounting in some cases to 30 per cent of their dry weight. In the land plants the potassium is present chiefly in the form of salts of organic acids. When such plants are burned, the potassium remains in the ash as carbonate, and the crude carbonate so obtained was formerly the chief source of potassium compounds. In recent years, except during the period of the World War, the Stassfurt deposits have constituted the chief source of these compounds.

**Stassfurt salts.** These salts, evidently deposited from sea water under peculiar geological conditions, form very extensive deposits in middle and north Germany, the most noted locality for working them being at Stassfurt. The deposits are very thick and rest upon an enormous layer of common salt. They are in the form of a series of strata, each consisting largely of a single mineral salt. Over thirty different minerals are present, but some are in very small quantities. Fig. 159

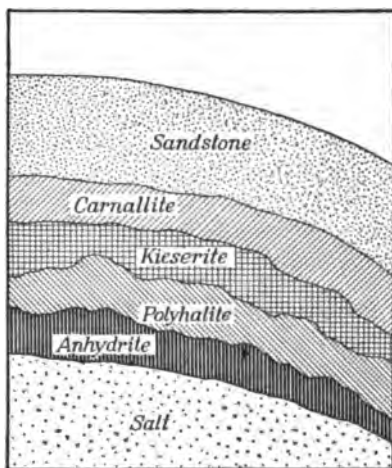


FIG. 159

shows a cross section of these deposits. While from a chemical standpoint these strata are salts, they are as solid and hard as many kinds of stone and are mined as stone or coal would be. Since the strata differ in general

appearance, each can be mined separately, and the various minerals can be worked up by methods adapted to each particular case. The chief minerals of commercial importance in these deposits are the following :

Sylvite . . .	KCl	Kainite . .	$\text{MgSO}_4 \cdot \text{KCl} \cdot 3 \text{H}_2\text{O}$
Anhydrite . .	$\text{CaSO}_4$	Kieserite .	$\text{MgSO}_4 \cdot \text{H}_2\text{O}$
Carnallite . .	$\text{KCl} \cdot \text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$	Schönite .	$\text{K}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 6 \text{H}_2\text{O}$

**Sources of potassium salts in the United States.** For a number of years previous to the World War practically the entire amount of potassium salts consumed in the United States was obtained from Germany. With the declaration of war, this supply was cut off and persistent efforts were made to develop an independent supply within our own borders sufficient to meet our needs, especially for making glass and fertilizers. As a result a limited amount was obtained from the following sources :

1. *Natural brines.* The waters of certain partially dried-up lakes located in Nebraska yield on evaporation a mixture of salts containing varying amounts of potassium sulfate and potassium carbonate. Searles Lake in California also furnished some potassium chloride. About three fourths of the potassium salts produced in the United States during the World War came from these sources.

2. *The great algae of the California coast.* These are rich in potassium chloride and constituted the source of a limited supply.

3. *Alunite.* Some potassium sulfate was also obtained from the mineral alunite ( $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 4 \text{Al}(\text{OH})_3$ ), which occurs in Utah.

4. Other minor sources were the dust from cement kilns, the wastes in the separation of sugar from plant juices, and wood ashes.

Previous to the war the United States imported yearly from Germany about 240,000 tons of potassium salts calculated as  $\text{K}_2\text{O}$ . The maximum production in the United States (1918) amounted to about one fourth of this. This production cannot continue in competition with Germany except by government aid.

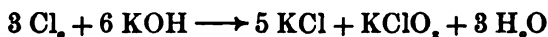
**Preparation and properties.** The metal can be obtained by the general method used in the preparation of sodium. This process, however, is more difficult to carry out, and, as the metal has no particular uses, but little of it is produced. It has a density of 0.862, melts at  $62.3^\circ$ , and boils at  $758^\circ$ . It is very similar to sodium, differing from it mainly in its greater activity. It decomposes water violently, the heat of the reaction being sufficient to ignite the hydrogen evolved. Under like conditions sodium melts but does not ignite the hydrogen.

**Compounds of potassium.** In a general way the compounds of potassium are similar to the corresponding ones of sodium and therefore will not be discussed in such detail. Many of the compounds volatilize when heated in a Bunsen flame, and impart to it a characteristic violet color, which serves to indicate the presence of the element. If other compounds which mask this color are present (for example, those of sodium), the flame may be examined through the spectroscope, the characteristic spectrum of potassium being easily recognized.

**Potassium hydroxide (caustic potash) (KOH).** This compound is prepared by the methods used in the production of sodium hydroxide. It is very soluble in water, the solution being strongly basic. Exposed to the air it rapidly absorbs water and is a good dehydrating agent. It is often used in the laboratory to remove both water and carbon dioxide from gases. It is not used to any great extent commercially, being replaced by the cheaper sodium hydroxide.

**Potassium halides.** Of these compounds *potassium chloride* is the most familiar, since it is found in such large quantities in the deposits of Stassfurt and Alsace. The mineral *sylvite* is nearly pure potassium chloride. The salt is obtained not only from sylvite but also from *carnallite* ( $\text{KCl} \cdot \text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$ ). When dissolved in water, carnallite separates into its constituent compounds, and advantage is taken of this fact in the preparation of potassium chloride. A hot saturated solution of the mineral is first prepared. When this is cooled, the potassium chloride, being less soluble than the magnesium chloride, crystallizes out. In its general properties potassium chloride resembles sodium chloride. It is used in the preparation of nearly all other potassium salts and as a fertilizer. *Potassium bromide* (KBr) is prepared by the action of bromine upon a hot solution of potassium hydroxide (p. 359). *Potassium iodide* (KI) is made in a similar manner. Both the iodide and bromide are used in medicine and in photography. *Potassium fluoride* is of interest in connection with the preparation of fluorine (p. 353).

**Potassium chlorate ( $\text{KClO}_3$ ).** This salt is formed by the action of chlorine upon warm solutions of potassium hydroxide (p. 373).



It will be noted, however, that the yield is very small, six molecules of the hydroxide giving but one of the chlorate. Commercially the yield is greatly improved by generating the chlorine and potassium hydroxide by the electrolysis of potassium chloride under such conditions that they react to form the chlorate according to the above equation. By continuing the process all the chloride is finally converted into the chlorate.

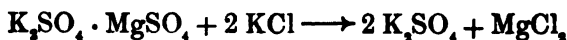
Another process used commercially consists in the action of potassium chloride upon calcium chlorate, the latter compound being prepared from calcium hydroxide (slaked lime) at very low cost:



It will be noted that all the potassium entering into the reaction is converted into the chlorate. The potassium chlorate is separated from the accompanying calcium chloride by evaporating the solution. The chlorate, being much less soluble than the calcium chloride, separates first.

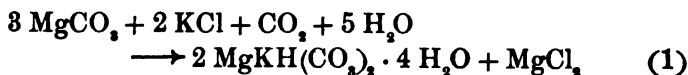
Potassium chlorate melts at  $370^\circ$ . When heated to a higher temperature, a portion of the compound is converted into potassium chloride and oxygen, while another portion is converted into potassium chloride and perchlorate (p. 374). When treated with hydrochloric acid, the oxygen of the chlorate unites with the hydrogen of the acid, thus liberating chlorine. This mixture may therefore be used in place of *aqua regia* as a solvent. The chief use of potassium chlorate is as an oxidizing agent in the manufacture of matches, fireworks, and explosives. It is also used in medicine and in the preparation of oxygen.

**Potassium sulfate ( $\text{K}_2\text{SO}_4$ ).** This salt is formed by the action of sulfuric acid upon potassium chloride. Commercially it is prepared from the Stassfurt salts, especially *schönite*, by the action of potassium chloride:

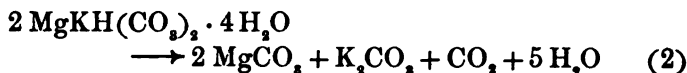


When the solution is evaporated, the resulting potassium sulfate, being much less soluble than the magnesium chloride, separates first. Potassium sulfate is used as a fertilizer and for making potassium aluminium sulfate (potash alum). When heated with sulfuric acid, it is converted into *potassium bisulfate*  $\text{KHSO}_4$ .

**Potassium carbonate ( $\text{K}_2\text{CO}_3$ ).** This compound can be prepared from potassium chloride by the Leblanc process, just as sodium carbonate is prepared from sodium chloride. Commercially it is chiefly prepared according to the reactions indicated in the following equations:



The resulting carbonate is decomposed when heated:



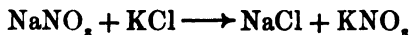
The magnesium carbonate and carbon dioxide formed according to equation (2) react with a further supply of potassium chloride according to equation (1), and the process thus continues. If equations (1) and (2) are combined, the resulting equation is as follows:  $\text{MgCO}_3 + 2 \text{KCl} \longrightarrow \text{MgCl}_2 + \text{K}_2\text{CO}_3$

This shows that magnesium carbonate and potassium chloride are the only substances used up in the reaction.

Potassium carbonate is used in the manufacture of glass and, to a limited extent, in the preparation of other compounds of potassium. When carbon dioxide is passed into a saturated solution of the carbonate, *potassium bicarbonate* ( $\text{KHCO}_3$ ) is formed. Both the carbonate and bicarbonate are very similar to the corresponding salts of sodium.

**Potassium nitrate (saltpeter) ( $\text{KNO}_3$ ).** This compound constituted one of the most important reagents of the alchemists. It is formed in the decay of nitrogenous organic matter (p. 276) and therefore accumulates in some regions where the climate is

hot and dry. At present it is prepared by the action of sodium nitrate upon potassium chloride :



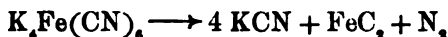
The sodium nitrate used in the process is obtained from the Chile niter beds and the potassium chloride from the Stassfurt salts.

The reaction depends for its success upon the apparently insignificant fact that sodium chloride is almost equally soluble in cold and in hot water. All four compounds represented in the equation are rather soluble in cold water, but in hot water sodium chloride is far less soluble than the other three. When hot saturated solutions of sodium nitrate and potassium chloride are brought together, sodium chloride reaches its solubility product first, precipitates, and can be filtered off, leaving potassium nitrate in solution, together with some sodium chloride. When cooled, potassium nitrate crystallizes out, leaving small amounts of the other salts in solution.

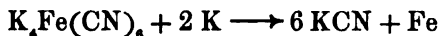
Potassium nitrate dissolves in water with marked absorption of heat. It crystallizes from water in large rhombic crystals, which melt at  $345^\circ$ . When heated alone it gives up oxygen, forming the nitrite. It was in this way that Scheele first obtained oxygen. It is an excellent oxidizing agent. Its chief use is in the manufacture of gunpowder; for this purpose it is preferable to sodium nitrate, since the latter is deliquescent, and powder made with it, if exposed to air, soon becomes unfit for use. Smaller amounts are used in medicine and as a preservative for meat.

**Gunpowder.** Gunpowder is an intimate mixture of potassium nitrate, charcoal, and sulfur. When ignited by a spark it burns explosively, forming a number of products, some of which are gases while others are solids. The gases constitute about 50 per cent by weight of the total products and consist principally of carbon monoxide, carbon dioxide, and nitrogen; while the principal solids formed are potassium carbonate, potassium sulfate, and potassium sulfide.

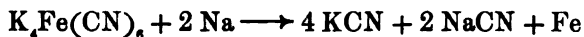
**Potassium cyanide (KCN).** Potassium cyanide is very similar to sodium cyanide in its properties. It is prepared from the compound known as potassium ferrocyanide ( $\text{K}_4\text{Fe}(\text{CN})_6$ ) (p. 628). When heated to a red heat potassium ferrocyanide decomposes, forming potassium cyanide, iron carbide, and nitrogen :



The yield is improved and a purer product obtained by heating a mixture of the ferrocyanide and potassium:



Since sodium is much cheaper than potassium, it is often used in place of it, the product being a mixture of the cyanides of sodium and potassium:



This mixture is known commercially as potassium cyanide. It was formerly used in extracting gold from its ores, but it has now been displaced by the cheaper sodium cyanide. Like sodium cyanide it is intensely poisonous.

With appropriate oxidizing agents potassium cyanide yields potassium cyanate ( $\text{KCNO}$ ); with sulfur it yields potassium sulfocyanate ( $\text{KCNS}$ ). The latter serves as a very delicate reagent for the detection of certain compounds of iron since it reacts with them to form the deep red sulfocyanate of iron ( $\text{Fe}(\text{CNS})_3$ ).

**Insoluble compounds of potassium.** The following compounds of potassium are but slightly soluble in water, so that the metal may be precipitated from its solutions in these forms: (1) *potassium perchlorate* ( $\text{KClO}_4$ ), a white, crystalline solid; (2) *potassium chloroplatinate* ( $\text{K}_2\text{PtCl}_6$ ), a yellow, crystalline solid; (3) *potassium sodium cobaltinitrite* ( $\text{K}_2\text{NaCo}(\text{NO}_2)_6$ ), a yellow, crystalline solid; (4) *potassium fluosilicate* ( $\text{K}_2\text{SiF}_6$ ), a white solid. The solubility of all these compounds is greatly decreased by the addition of alcohol.

**Sodium compounds and potassium compounds contrasted.** The compounds of sodium and potassium are not only alike in composition but so nearly resemble each other in properties that, for the great majority of uses, it is immaterial which of the two corresponding compounds is employed. Thus, for an operation requiring a strong base, we may employ either sodium hydroxide or potassium hydroxide. Other things being equal, the cheaper compound will be selected. Since the natural compounds of sodium are much more readily available than those of potassium, we should expect the compounds of sodium to be less expensive and therefore more generally used, and this is true. However, it must be remembered that the cost of a compound depends not only on the availability of raw materials but also upon the cost of the operation required to produce the compound. Now it is generally true that the salts of sodium are more soluble than

those of potassium. They are, therefore, often more difficult to obtain in a pure state since their greater solubility makes it more difficult to purify them. For this reason potassium chlorate is more readily obtained pure than sodium chlorate. Again, the compounds of sodium are more deliquescent than those of potassium, and this difference sometimes influences the choice. Thus, potassium nitrate is used for making gunpowder in preference to the cheaper sodium nitrate.

Furthermore, an examination of the formulas of the compounds of sodium and potassium will show that more of the former contain water of crystallization than the latter, and this may enter into the choice of compounds.

### RUBIDIUM AND CÆSIUM

These two elements were discovered by Bunsen while making a spectroscopic examination of the residues from certain mineral waters. The characteristic lines in the spectrum of the one are red in color, while those of the other are blue; hence the names *rubidium*, meaning "dark red," and *cæsium*, meaning "blue."

Rubidium and cæsium are usually associated with potassium, although present in very small quantities. Rubidium is absorbed from the soil by certain plants, especially the sugar beet and tobacco. Cæsium occurs on the island of Elba and in New England in the form of the very rare mineral known as *pollucite*, which is a cæsium aluminium silicate.

The free metals are very difficult to prepare; their most important properties have been given in the table at the beginning of the chapter. They form compounds analogous in formulas and general properties to those of sodium and potassium. Because of their high cost neither the metals nor their compounds have any commercial uses.

### COMPOUNDS OF AMMONIUM

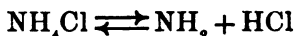
**General.** As explained in Chapter XVII, when ammonia is passed into water, the two unite to form the base ammonium hydroxide, and when this base is neutralized with acids, ammonium salts are formed. Since the ammonium group is univalent, ammonium salts resemble those of the alkali metals in formulas; they also resemble the latter salts in their chemical properties, and may be conveniently described in connection with them. They all volatilize upon being heated, most of them being decomposed in the process. When heated with an aqueous solution of sodium hydroxide, they evolve ammonia (p. 251). Since

the ammonia can be easily recognized, the reaction serves for the detection of the presence of ammonium compounds.

**Occurrence.** Small quantities of ammonium compounds are found in the soil. They are being continually absorbed by growing plants, but are returned to it again in the process of decay. They are also found in sea water and in some volcanic regions. Larger quantities are found in the Stassfurt deposits. Commercially in the United States all ammonium compounds are still largely prepared from the ammoniacal liquors produced in the manufacture of coke and coal gas (p. 252), although synthetic methods promise to come into use.

**Ammonium chloride (sal ammoniac) ( $\text{NH}_4\text{Cl}$ ).** This compound was known and used by the ancients, who obtained it by burning animal excrement. It is prepared commercially by treating the ammoniacal liquors of the gas works and by-product coke ovens with lime and passing into hydrochloric acid the ammonia which is evolved. By evaporating the resulting solution the impure salt is obtained. This is purified by sublimation.

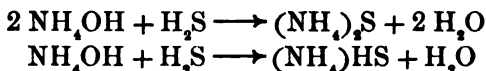
The density of the vapor obtained by heating ammonium chloride is only about half what one would expect if the vapor consisted of molecules of the salt. Experiments have shown that this apparent discrepancy is due to the fact that at high temperatures the salt is dissociated into ammonia and hydrogen chloride, which, however, recombine as the temperature falls:



The salt is used in soldering, since the hydrogen chloride evolved in the process removes any oxide from the surface of the metals. It is also used in medicine, in the preparation of ammonia, in making dry cells, and as a chemical reagent.

**Other ammonium halides.** These resemble ammonium chloride in their general properties. The iodide  $\text{NH}_4\text{I}$  readily absorbs moisture upon exposure to air and decomposes to such an extent that the free iodine liberated colors the salt. The fluoride  $(\text{NH}_4)_2\text{F}_2$  attacks silicates and is used for etching upon glass. The bromide and iodide are used in photography.

**Ammonium sulfides.** The normal sulfide  $(\text{NH}_4)_2\text{S}$  and the acid sulfide  $(\text{NH}_4)\text{HS}$  are formed when hydrogen sulfide and ammonia are brought together in the proper proportions at temperatures below zero. They form colorless crystals which dissociate into ammonia and hydrogen sulfide as the temperature rises. In solution they are formed by passing hydrogen sulfide into aqua ammonia:



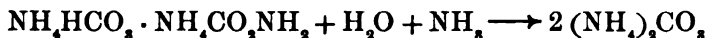
The normal salt, however, is almost completely hydrolyzed in solution, forming the acid sulfide and ammonium hydroxide.

The solution obtained by passing hydrogen sulfide into aqua ammonia, and commonly known as ammonium sulfide, is largely used in the laboratory as a reagent in the precipitation of certain metals. When exposed to air this solution gradually decomposes, the hydrogen sulfide formed in the hydrolysis being oxidized to water and sulfur. The sulfur, however, does not separate but combines with the compounds present, forming several different sulfides, such as  $(\text{NH}_4)_2\text{S}_2$ ,  $(\text{NH}_4)_2\text{S}_3$ ,  $(\text{NH}_4)_2\text{S}_4$ . The resulting solution is yellow in color and is known as *ammonium polysulfide*, or yellow ammonium sulfide. It is used in the laboratory as a solvent for the sulfides of arsenic, antimony, and tin. It can be prepared by adding sulfur to a solution of ordinary ammonium sulfide. Some of the individual polysulfides have been obtained in the form of pure crystals that are fairly stable.

**Ammonium sulfate  $(\text{NH}_4)_2\text{SO}_4$ .** This is one of the cheapest and most widely used of the ammonium salts. It is prepared by passing ammonia into sulfuric acid and is largely used as a fertilizer. By the action of sulfuric acid it is changed into the bisulfate  $\text{NH}_4\text{HSO}_4$ ; this upon electrolysis yields ammonium persulfate  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ , which is used as an oxidizing agent.

**Ammonium carbonates.** When a mixture of limestone  $(\text{CaCO}_3)$  and ammonium chloride is heated, there is formed as a sublimate a compound which is made up of ammonium bicarbonate and ammonium carbamate (p. 383) and has the formula  $\text{NH}_4\text{HCO}_3 \cdot \text{NH}_4\text{CO}_2\text{NH}_2$ . This salt is known as *commercial ammonium carbonate*. When ammonia is passed into a

concentrated aqueous solution of this salt, the normal ammonium carbonate  $(\text{NH}_4)_2\text{CO}_3$  is formed and, being but slightly soluble in strong ammonia water, separates as a white crystalline solid:



The normal carbonate is unstable, decomposing at ordinary temperatures with evolution of ammonia:



The bicarbonate  $\text{NH}_4\text{HCO}_3$  is much more stable. It is prepared by passing carbon dioxide into aqua ammonia. When heated sufficiently it is decomposed into water and the gases ammonia and carbon dioxide, so that it is sometimes used as an aërating agent in making certain forms of pastry. A solution of the carbonates is used in the laboratory in reactions requiring a soluble carbonate.

**Ammonium nitrate  $(\text{NH}_4\text{NO}_3)$ .** This salt may be prepared by the action of nitric acid upon either ammonium hydroxide or carbonate or by the partial oxidation of ammonia (p. 566). It is used in the preparation of nitrous oxide (p. 272) and as a constituent of certain explosives. For example, the explosive *ammonal*, so largely used in the World War, consisted of ammonium nitrate and powdered aluminium; sometimes varying amounts of potassium nitrate and charcoal are added.

### QUESTIONS

1. (a) Write the equation for the reaction between lithium and water. (b) How could you prepare lithium carbonate from the chloride?
2. What effect would you expect solutions of the following compounds to have on litmus:  $\text{NaCl}$ ,  $\text{K}_2\text{CO}_3$ ,  $\text{Na}_3\text{PO}_4$ ,  $\text{Na}_2\text{S}$ ?
3. Is the term *hyposulfite of soda* as applied to the compound  $\text{Na}_2\text{S}_2\text{O}_3$  correctly used?
4. Suggest a reason why cream of tartar baking powders are no longer used to any very great extent.
5. Write the equation for the preparation of potassium bromide and potassium iodide.

6. (a) How could you prepare potassium chloride from potassium sulfate? (b) potassium iodide from potassium chloride?

7. What substances have we studied that are prepared from the following compounds: ammonium nitrate, ammonium nitrite, ammonium chloride, potassium chlorate, potassium hydroxide, sodium chloride?

8. Assuming that sodium chlorate and potassium chlorate cost the same per pound, and that each gave up its oxygen with equal ease, which would be the more economical oxidizing agent to use?

9. Name the different compounds so far studied, that are used as explosives.

### PROBLEMS

1. When treated with water, what volume of oxygen will 1 kg. of sodium peroxide evolve at 20° and 740 mm.?

2. Suppose you wished to prepare 100 kg. of potassium iodide. What raw materials and what weights of each would you require?

3. Assuming that the yield obtained is 95 per cent of the theoretical, calculate the daily consumption of sodium chloride in a plant that produces 10 tons of soda ash daily.

4. (a) In what proportions must cream of tartar and baking soda be mixed in a baking powder? (b) What volume of carbon dioxide at 100° and 760 mm. would 25 g. of such a mixture evolve?

5. What weight of potassium chloride is required to make 100 kg. of caustic potash?

6. What weight of soda ash will 50 kg. of sodium bicarbonate yield?

7. What weight of sal soda will 100 lb. of soda ash yield?

## CHAPTER XXXIV

### THE ALKALINE EARTH METALS

	ATOMIC WEIGHT	DENSITY	MELTING POINT	FORMULA OF CHLORIDE
Calcium (Ca) . . . . .	40.07	1.55	810°	$\text{CaCl}_2$
Strontium (Sr) . . . . .	87.63	2.54	?	$\text{SrCl}_2$
Barium (Ba) . . . . .	137.37	3.75	850°	$\text{BaCl}_2$

The family. Calcium, strontium, and barium are known as the alkaline earth metals. Together with radium they constitute one of the families in Group II of the periodic table. While radium closely resembles barium, it is more convenient to discuss it in connection with uranium, to which it bears a peculiar relation. The term *alkaline earths* was originally applied to the oxides of these metals because they bore some resemblance both to the alkalis and to the earths, the latter being a general term for such oxides as those of iron and aluminium. As in the case of the alkalis, the alkaline earths were thought to be elementary in character until 1807, when Davy succeeded in decomposing them just as he had decomposed the alkalis.

In a lecture delivered on June 30, 1808, before the English Royal Society, Davy refers to his discovery as follows: "The evidence for the composition of the alkaline earths is then of the same kind as that for the composition of the common metallic oxides; and the principles of their decomposition are precisely similar. . . . These new substances will demand new names; and on the same principles as I have named the bases of the fixed alkalis I shall venture to denominate the metals from the alkaline earths barium, strontium, calcium. . . ."

The alkaline earth metals are light, active elements. They form compounds in which the metal acts as a bivalent element. Unlike the alkali metals their normal carbonates, phosphates,

and silicates are insoluble in water. Barium sulfate is also insoluble, while the sulfates of calcium and strontium are but sparingly soluble.

### CALCIUM

**Occurrence.** Compounds of calcium are found in large quantities in various regions. The most abundant of these compounds is the carbonate, which occurs in many different forms, such as *marble* and *limestone*. Other calcium-bearing minerals are the following: *fluorapatite* ( $3 \text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaF}_2$ ), *chlorapatite* ( $3 \text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaCl}_2$ ), *fluorite* ( $\text{CaF}_2$ ), *wollastonite* ( $\text{CaSiO}_3$ ), *gypsum* ( $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$ ), *anhydrite* ( $\text{CaSO}_4$ ), and *phosphorite* ( $\text{Ca}_3(\text{PO}_4)_2$ ).

**Preparation.** Davy first isolated calcium by the electrolysis of the hydroxide. It is now prepared by the electrolysis of the melted chloride, and a number of different cells have been devised for effecting the electrolysis.

#### Method of Seward and von Kugelgen.

One form of cell for the commercial production of calcium is represented in Fig. 160. It consists of a cylindrical iron vessel, through the bottom of which extends the iron cathode *A*. The anodes *B, B*, several in number, are distributed about the sides of the vessel. The calcium separates at the cathode in a molten condition and rises in the form of globules to the lower surface of a solid stick of calcium *D*, suspended above the cathode, as shown in the diagram. There it be-

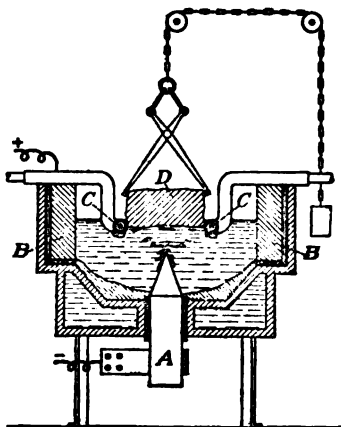
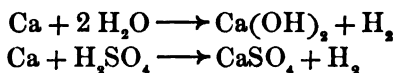


FIG. 160

comes chilled by a water-cooling device *C, C* and adheres to the stick of calcium, which is slowly raised as it increases in length.

**Properties.** Calcium is a silvery white metal, but acquires a slightly yellowish tinge upon exposure to air, owing to its union with nitrogen. It has a density of 1.55 and melts at  $810^\circ$ . It combines readily with most of the nonmetals, often with evolution

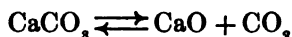
of light. For example, it combines with the elements of the sulfur family, the chlorine family, and the nitrogen family (bismuth excepted). When heated to ignition in oxygen, it burns with dazzling brilliancy. When burned in air, both the oxide and the nitride of calcium are obtained. It reacts with water and with dilute acids, as represented in the following equations:



Calcium promises to become a useful metal, although its commercial applications are as yet rather limited. It is a powerful reducing agent and would undoubtedly find application in the reduction of some of the metallic oxides if it could be produced at a sufficiently low cost.

**Compounds of calcium.** The preparation of the compounds of calcium does not in general present as great a problem as does the preparation of those of sodium. This is due to the fact that the form in which calcium occurs most abundantly in nature is the carbonate, a compound which is readily changed into other compounds by the action of the appropriate acids. Moreover, the carbonate can be decomposed by heat without difficulty, thus furnishing an inexpensive method for the preparation of the oxide (lime).

**Calcium oxide (lime) (CaO).** Calcium oxide may be obtained by burning the metal in air or by heating the nitrate or carbonate. It is obtained commercially by heating limestone in large furnaces called limekilns:

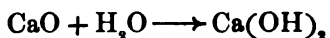


The reaction is reversible, as is indicated in the equation. If the decomposition is carried out in a closed vessel, equilibrium between the opposing reactions is reached at any definite temperature when the dissociation pressure reaches a definite value (p. 288). The higher the temperature the greater the pressure at equilibrium, as shown in the following table, in which the pressure is expressed in millimeters of mercury:

Temperature,	547°	610°	625°	740°	745°	810°	812°	865°
Pressure,	27	46	46	225	289	678	753	1333

If, on the other hand, the carbon dioxide is conducted away as fast as formed, the decomposition will continue until complete. This is the method adopted in the production of lime, the limestone being heated in a current of air, which carries away the carbon dioxide.

Pure calcium oxide is a white, amorphous substance, the density of different specimens varying from 3 to 3.3. When heated intensely, as in the oxyhydrogen blowpipe, it gives a brilliant light. Although it is a substance very difficult to fuse, it not only melts but boils vigorously at the temperature of the electric furnace (about  $3500^{\circ}$ ). Water acts upon lime, with the evolution of considerable heat, the process being called *slaking*.



When exposed to air, calcium oxide is gradually converted into the hydroxide and carbonate and will no longer slake upon addition of water. It is then said to be air-slaked. Lime is produced in enormous quantities and is used in making calcium hydroxide.

#### Commercial production of lime.

The older form of kiln, still in use, consists of a large stack, or chimney, in which the limestone is loosely packed. A fire is built at the base of the stack, and when the decomposition of the limestone is complete, the fire is allowed to die out and the lime is removed. A vertical section of the newer form of kiln is shown in Fig. 161. The kiln is about 50 ft. in height. A number of fire boxes

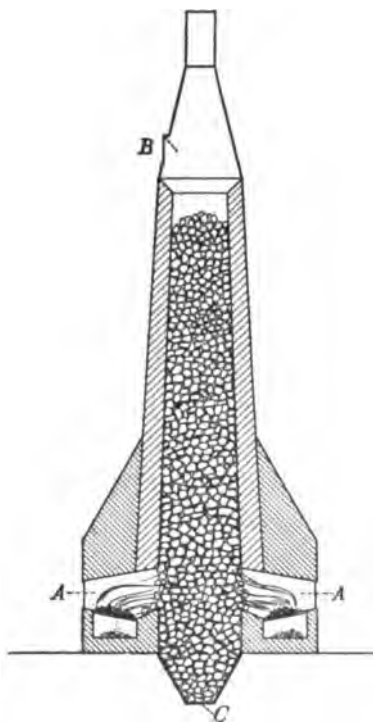


FIG. 161

or furnaces *A, A* are built around the lower part, all leading into the central stack. The kiln is filled with limestone through a swinging door *B*. The hot products of combustion are drawn up through the kiln, and the limestone

is gradually decomposed by the heat. The bottom of the furnace is so constructed that a current of air is drawn in at *C*, and this serves the double purpose of cooling the hot lime at the base of the furnace and furnishing heated oxygen for the combustion. The lime is dropped into cars run under the furnace. The advantage of this kind of kiln over the older form is that the process is continuous, limestone being charged in at the top as fast as the lime is removed at the bottom.

**Calcium hydroxide (slaked lime, hydrated lime)  $(\text{Ca}(\text{OH})_2)$ .** This compound is prepared by adding water to calcium oxide. Considerable heat is developed in the reaction, as is represented in the following equation :



The reaction is reversible, the decomposition of the hydroxide into its components taking place rapidly when heated in an open vessel to a temperature above  $450^\circ$ . Pure calcium hydroxide is a white powder having a density of about 2. It is but slightly soluble in water, its solubility diminishing with rise in temperature. Thus, at  $10^\circ$ , 1 l. of water dissolves 1.76 g. of the hydroxide; at  $50^\circ$ , 1.28 g.; and at  $100^\circ$ , only 0.77 g. Its solution in water is termed *limewater* and is often used in medicine because of its basic properties. Calcium hydroxide is a moderately strong base and, owing to its cheapness, is much used in the industries whenever an alkali is desired. A number of its uses have already been mentioned. It is used in the preparation of ammonia, bleaching powder, and the hydroxides of sodium and potassium. It is also used in the purification of coal gas (p. 417), in removing the hair from hides, in the manufacture of leather, and in making mortar and plaster. Acid soils are treated with the hydroxide to neutralize the acid present.

**Mortar.** Ordinary mortar is a mixture of calcium hydroxide and sand. When it is exposed to the air or spread upon porous materials, it loses moisture, chiefly by evaporation, and the mortar becomes firm, or *sets*. At the same time carbon dioxide is slowly absorbed from the air, and hard calcium carbonate is formed :



By this combined action the mortar becomes very hard and adheres firmly to the surface upon which it is spread. The sand serves to give body to the mortar and makes it porous. It also prevents too much shrinkage.

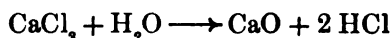
**Sulfides of calcium.** The normal sulfide  $\text{CaS}$  is prepared by reducing calcium sulfate with carbon. It is obtained as a by-product in the Leblanc process for the manufacture of sodium carbonate. Although insoluble in water, it gradually undergoes hydrolysis, forming the acid sulfide  $(\text{Ca}(\text{HS})_2)$ , which is soluble. A mixture of the tetrasulfide  $\text{CaS}_4$  and pentasulfide  $\text{CaS}_5$  can be obtained by heating calcium hydroxide and sulfur in the presence of water, and a solution of these sulfides constitutes the ordinary *lime sulfur spray*.

The normal sulfide as prepared commercially is sometimes used as a pigment for luminous paint, since after exposure to a bright light it will glow in the dark. It is interesting to note that the pure sulfide does not possess this property, but acquires it in the presence of small percentages of the sulfides of some other metals, especially those of manganese, bismuth, and vanadium.

**Calcium fluoride ( $\text{CaF}_2$ ).** This salt occurs in large quantities in nature as *fluorite*. The mineral crystallizes in the form of cubes or octahedra, and large crystals are often found that are beautifully tinted, generally a shade of green or blue. When heated gently they become fluorescent. Calcium fluoride also occurs in the ashes of some plants. When pure it is a white solid and is nearly insoluble in water. It melts at  $1330^\circ$ . The mineral fluorite is mined in large quantities, especially in southern Illinois and Kentucky, and increasing amounts of it are being used as a flux in various metallurgical operations. It is also used in the manufacture of opaque glass and white enamel and in the preparation of other fluorine compounds, especially hydrofluoric acid.

**Calcium chloride ( $\text{CaCl}_2$ ).** This salt is present in sea water to a limited extent. Small quantities also occur as a constituent of some minerals, such as *tachhydrite* ( $2 \text{MgCl}_2 \cdot \text{CaCl}_2 \cdot 12 \text{H}_2\text{O}$ ), found in the Stassfurt deposits. It is formed in large quantities as a by-product in the manufacture of sodium carbonate by the Solvay process, as well as in the preparation of potassium chlorate from calcium chlorate. The mother liquor from salt works also contains a considerable percentage of the compound. The supply

of the compound obtained from these sources is at present much greater than the demand. Pure calcium chloride may be prepared by dissolving calcium carbonate in hydrochloric acid and evaporating to crystallization. It separates from saturated solutions at ordinary temperatures in the form of hexagonal crystals, which have the formula  $\text{CaCl}_2 \cdot 6 \text{H}_2\text{O}$ . The mono-, di-, and tetra-hydrates have also been prepared. When the hydrates are heated above  $260^\circ$ , the anhydrous salt is obtained as a white, porous mass. In this process some calcium oxide is formed by the action of water upon the chloride:



As a rule, therefore, a solution of the anhydrous salt reacts basic, owing to the presence of calcium hydroxide.

The anhydrous salt readily absorbs moisture and is largely used as a drying agent (p. 50). It melts at  $780^\circ$ . It dissolves in water with the liberation of considerable heat, while the hexahydrate absorbs heat under the same conditions. It is very soluble, 100 g. of water dissolving 59.5 g. at  $0^\circ$ . Owing to its great solubility, the boiling point of a concentrated solution of calcium chloride is much higher than that of water; thus, a solution containing 101 g. of the chloride in 100 g. of water boils at  $130^\circ$ . The solid hexahydrate and ice form a freezing mixture by means of which a temperature as low as  $-50^\circ$  can be reached. A solution of calcium chloride is largely used as a brine in the manufacture of artificial ice (p. 257). Because of its deliquescent character it has been used to lay the dust on roads. Mines have also been sprinkled with its solution in the hope of preventing dust explosions (p. 429).

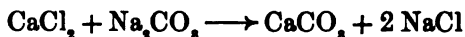
**Calcium carbonate ( $\text{CaCO}_3$ ).** Enormous quantities of calcium carbonate occur in nature. *Limestone* is the most abundant form and is a grayish rock usually found in hard, stratified masses. Whole mountain ranges are sometimes made up of this material. It is never pure calcium carbonate, always containing variable percentages of foreign matter, usually magnesium carbonate, clay,

silica, compounds of iron and aluminium, and frequently fossil remains. *Marl* is a mixture of limestone and clay. *Pearls, coral,* and various kinds of *shells*, such as eggshells and oyster shells, and *natural chalk* (not the blackboard crayon) are largely calcium carbonate.

Calcium carbonate is a dimorphous substance. The more common form of crystal belongs to the hexagonal system. *Calcite* is a pure, crystalline form of this character. Very beautiful transparent crystals of calcite are found in Iceland; hence the name *Iceland spar*, often applied to this variety. *Mexican onyx* is a massive variety streaked or banded with colors occasioned by impurities. *Marble* is made up of minute snow-white calcite crystals and was probably formed by the crystallization of the melted rock under great pressure. *Stalactites* and *stalagmites* are icicle-like forms sometimes found in caves.

Calcium carbonate is also found in nature in the form of crystals belonging to the rhombic system. The mineral *aragonite* is an example of this form. When heated it is transformed into a mass of calcite crystals. This transformation is probably taking place at ordinary temperatures but with a very low speed. It is easy to understand, therefore, why the aragonite form is a rather uncommon variety.

**Preparation and uses of calcium carbonate.** In the laboratory pure calcium carbonate can be prepared by precipitation:



When the precipitation is effected at ordinary temperatures, the carbonate is obtained as an amorphous powder which soon changes over into calcite crystals. When precipitated from hot dilute solutions, aragonite crystals are obtained, but these slowly change into the calcite form.

Pure calcium carbonate is very slightly soluble in water, 1 l. of water at 15° dissolving but 13 mg., or if it is in the form of aragonite, 15 mg. The action of acids upon this substance, as well as the effect of heat upon it, has already been discussed.

The natural varieties of calcium carbonate find many uses, such as in the preparation of lime, cement, in metallurgical operations (especially in blast furnaces), in the manufacture of soda and glass, and for building stone and ballast for roads.

Calcium acid carbonate (calcium bicarbonate) ( $\text{Ca}(\text{HCO}_3)_2$ ). While calcium carbonate is almost insoluble in pure water, it readily dissolves in water containing carbon dioxide. This is due to the formation of the soluble but unstable calcium acid carbonate. When solutions containing the acid carbonate are heated, the normal carbonate is precipitated (p. 383):



Natural waters always contain more or less carbon dioxide in solution. In the case of certain underground waters the amount of carbon dioxide is comparatively large, since it is held in solution by pressure. Such waters have a marked solvent action upon limestone, dissolving both the calcium carbonate and the magnesium carbonate. In certain localities this solvent action, continued through geological ages, has resulted in the formation of large caves in limestone rock, such as the Mammoth Cave in Kentucky.

Calcium sulfate ( $\text{CaSO}_4$ ). This compound occurs in nature in the anhydrous form in the mineral *anhydrite*. More commonly, however, it is found as *gypsum*, which is a dihydrate ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ). Several other varieties of gypsum are known, such as *selenite*, *alabaster*, and *satin spar*. When the dihydrate is heated, there is formed a hydrate of the formula  $2\text{CaSO}_4 \cdot \text{H}_2\text{O}$ . Since this compound contains half as many molecules of water of crystallization as of calcium sulfate, it is called a hemihydrate.

Of the different forms of calcium sulfate, gypsum is by far the most important commercially. It is quarried in large quantities, especially in New York, Iowa, and Michigan. It crystallizes in prismatic form belonging to the monoclinic system. It is but slightly soluble in water, its solubility increasing slowly from  $0^\circ$  to about  $35^\circ$  and then decreasing. It is used in making plaster of Paris, as a filler in making paper, as a paint pigment, and as a constituent of fertilizers. Its value as a fertilizer seems to be due to the fact that it reacts with the ammonium

carbonate present in the soil, forming ammonium sulfate, which is much less volatile than the carbonate and is therefore retained in the soil until taken up by the growing plants.

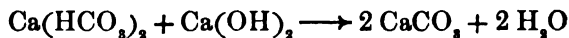
**Plaster of Paris.** This is a fine white powder obtained by heating gypsum, and consists essentially of the hemihydrate  $2 \text{CaSO}_4 \cdot \text{H}_2\text{O}$ . When water is added, this powder forms a plastic mass, which quickly hardens, or sets, and regains its crystalline structure. These properties make it valuable as a material for molding casts and stucco work, for cementing glass to metals, and for a finishing coat on plastered walls. When mixed with paper pulp and allowed to set in the form of boards, it forms a material much used in the construction of buildings, especially in place of plaster.

**Hard water.** Waters containing compounds of calcium and magnesium in solution are called hard waters for the reason that these salts precipitate soap and so interfere with its use (p. 455). The hardness of water may be of two kinds: (1) temporary hardness and (2) permanent hardness.

1. **Temporary hardness.** We have seen that when water charged with carbon dioxide comes in contact with limestone, a certain amount of the latter dissolves, owing to the formation of the soluble acid carbonate of calcium. The hardness of such waters is said to be temporary, since it may be removed by boiling. The heat changes the acid carbonate into the insoluble normal carbonate which then precipitates, rendering the water soft:

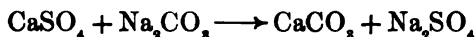


Such waters may also be softened by the addition of sufficient lime or calcium hydroxide to convert the acid carbonate of calcium into the normal carbonate:



2. **Permanent hardness.** The hardness of water may also be due to the presence of calcium and magnesium sulfates or chlorides. Boiling the water does not affect these salts; hence such waters are said to have permanent hardness. They may be softened,

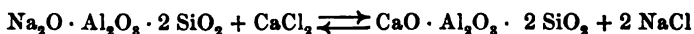
however, by the addition of sodium carbonate, which precipitates the calcium and magnesium as insoluble carbonates:



This process is sometimes called "breaking" the water.

**Commercial methods for softening water.** The average water of a city supply contains not only the acid carbonates of calcium and magnesium but also the sulfates and chlorides of these metals, together with other salts in smaller quantities. Such waters are softened on a commercial scale by the addition of the proper quantities of calcium hydroxide and sodium carbonate. The calcium hydroxide precipitates the acid carbonates, while the sodium carbonate precipitates the other soluble salts of calcium and magnesium. The amounts of calcium hydroxide and sodium carbonate required to soften any given water are calculated from a chemical analysis of the water. It will be noticed from the equations that the water softened in this way contains sodium sulfate and chloride, but the presence of these salts is not objectionable.

**The permutite process for softening water.** The term *permutite* is given to a mixture of complex sodium aluminium silicates prepared for use in softening water on a moderately large scale. This substance is characterized by the fact that the sodium present in the silicates is replaced by calcium and magnesium when brought in contact with solutions of these compounds:

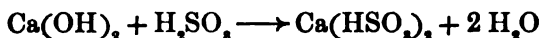


If, now, a concentrated solution of sodium chloride is allowed to flow over the resulting calcium compound, the reaction is reversed and the permutite regenerated. In other words, the reaction is reversible and may be made to go in either direction by increasing the mass of the appropriate compound. In softening water by this process the permutite is placed in a long drum and the water passed through the drum. The apparatus is built in duplicate, so that the material in the one drum may be regenerated while that in the other drum is being used for softening the water. It is evident that water softened in this way will contain sodium salts, but these have no effect on soap.

**Sulfitcs of calcium.** The normal sulfite  $\text{CaSO}_3$ , being but slightly soluble, is formed as a white precipitate when a solution of sodium sulfite is added to a solution of a calcium salt. When it is suspended in water and sulfur dioxide is passed into the mixture, it dissolves, owing to the formation of the soluble bisulfite  $\text{Ca}(\text{HSO}_3)_2$ . A solution of this bisulfite with some free

sulfurous acid is used in large quantities in the manufacture of paper (p. 811). Two methods are used for its preparation on a large scale:

1. Sulfur dioxide is passed into a solution of calcium hydroxide:



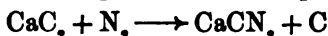
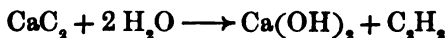
2. Sulfur dioxide is passed upwards through large towers filled with limestone over which water trickles:



**Calcium carbide ( $\text{CaC}_2$ ).** This compound is now prepared on a large scale for use in generating acetylene (p. 411) and in making fertilizer. It was first obtained in impure form by E. Davy in 1836, and by Wöhler in 1863. Later, Borchers and also Moissan obtained it in pure crystalline form. In 1893 Wilson, an American chemist, devised a method for preparing it on a large scale, and since that time it has been a commercial product. It is made by heating a mixture of coke and lime in an electric furnace:



The pure carbide is a colorless, transparent, crystalline substance and is practically insoluble in all known solvents. At high temperatures it is a powerful reducing agent. Its commercial importance lies in the fact that it reacts with water to form acetylene and with nitrogen to form calcium cyanamide ( $\text{CaCN}_2$ ).



The commercial article is a dull-gray, porous substance which contains many impurities. The acetylene prepared from this substance has a disagreeable odor due to phosphine and other impurities.

**Commercial production of calcium carbide.** The general form of furnace used for making calcium carbide on a large scale is shown in Fig. 162. The sides and bottom of the furnace are built of brick and large carbon electrodes

*A, A, A* extend into the furnace. The furnace is nearly filled with a mixture of coke and lime *B, B*. The current is then connected and regulated so as to secure a temperature of about 2000°. At this temperature the carbide gradually forms. As the temperature is above its melting point, it separates in liquid form *C, C, C, C* and is drawn off at the outlet *D*. The process is continuous, the raw materials being added from time to time as the carbide is withdrawn. These furnaces are really large brick rooms.

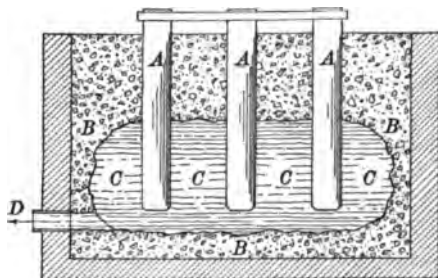
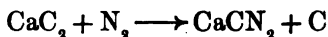


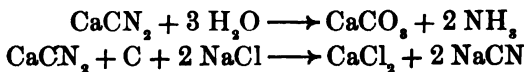
FIG. 162

**Calcium cyanamide ( $\text{CaCN}_2$ ).** This compound is formed when nitrogen is passed over calcium carbide heated to about 1200°:



The compound is a derivative of *cyanamide* ( $\text{H}_2\text{CN}_2$ ), the two hydrogen atoms of the cyanamide being replaced by the bivalent calcium atom. The commercial product contains about 60 per cent of the cyanamide; the remaining 40 per cent consists chiefly of carbon and lime. The product is known as *lime-nitrogen*. This is ground and mixed with water (which slakes the lime) and in this form is sold as a fertilizer under the name *cyanamide*. Its value as a fertilizer lies in the fact that all of its nitrogen is available as a plant food.

Calcium cyanamide promises also to become of importance in the commercial preparation of ammonia and sodium cyanide, both of which can readily be obtained from it in a manner indicated by the following equations:



The nitrogen used in the preparation of the cyanamide is obtained from liquid air (p. 97). By means of the above reactions it is possible, therefore, to convert the nitrogen of the air into important compounds of nitrogen.

**Nitrogen fixation.** References have been made under various headings to the methods which are either being used or tested for utilizing the nitrogen of the atmosphere by converting it into useful compounds. It is desirable to bring these methods together in one place. They are as follows:

1. *The arc process* (p. 262), which results in the formation of nitric acid.
2. *The cyanamide process* (described above), which yields calcium cyanamide, which in turn serves for the preparation of ammonia or metallic cyanides.
3. *The Haber process* (p. 250), which gives ammonia by direct synthesis.
4. *The nitride process* (p. 254), which consists in heating certain metals, especially aluminium, with nitrogen. Upon treating the resulting nitrides with water, ammonia is evolved.
5. *The Bucher process* (p. 539), which yields sodium cyanide.

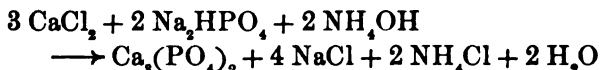
The first three of these methods are now used commercially, and it is reasonably certain that the resulting compounds, or similar ones derived from atmospheric nitrogen, will eventually replace the sodium nitrate and ammonium salts which are now obtained from other sources and used in the manufacture of nitric acid and fertilizers.

Reference has been made to the fact that during the World War Germany used the Haber process for making ammonia, which in turn was converted into nitric acid by oxidation with air (p. 262). As soon as the United States entered the war steps were taken to build government plants for the production of nitric acid from atmospheric nitrogen, so that we should be independent of the supply of sodium nitrate from Chile, if for any reason that supply were cut off. Four of these plants were authorized, as follows: (1) Plant No. 1, located at Sheffield, Alabama, for the manufacture of ammonia by a modified Haber process; (2) Plant No. 2, located at Muscle Shoals, Alabama, for making calcium cyanamide; (3) and (4) Plants No. 3 and 4, located at Toledo and near Cincinnati, Ohio, respectively, for the manufacture of calcium cyanamide. Of these, only Plant No. 2 came into operation before the signing of the armistice. The cyanamide produced was converted into ammonia and a part of this into nitric acid. By combining the two, ammonium nitrate was obtained and the output of the plant was in this form. The capacity of the plant was three hundred tons of the nitrate per day.

**Phosphates of calcium.** With phosphoric acid, calcium forms three salts, the names and formulas of which are as follows:

Normal (or tertiary) calcium phosphate . . .	$\text{Ca}_3(\text{PO}_4)_2$
Secondary calcium phosphate . . . . .	$\text{CaHPO}_4$
Primary calcium phosphate . . . . .	$\text{Ca}(\text{H}_2\text{PO}_4)_2$

The normal phosphate, usually called simply calcium phosphate, is found in quantities in nature, largely in the form of *phosphorite*. It is the chief mineral constituent of bones, the ash of which contains about 80 per cent of this compound. It can be obtained by adding ammonium hydroxide to a solution of a calcium salt until strongly alkaline, and then precipitating with disodium phosphate:

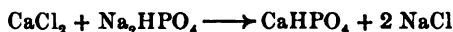


It is nearly insoluble in water but easily dissolves in acids, even in very weak ones like acetic acid. The importance of the phosphates in connection with the subject of fertilizers has already been discussed (p. 470).

Primary calcium phosphate is deposited in the form of white crystals when a solution of the normal phosphate in phosphoric acid is evaporated:



When a solution of disodium phosphate is added to a solution of a calcium salt, secondary calcium phosphate is obtained:



Both of the acid salts are also formed, along with calcium sulfate, by the action of sulfuric acid upon normal calcium phosphate (p. 471).

**Silicates of calcium.** A number of these are known. The metasilicate  $\text{CaSiO}_3$  occurs pure in nature in the form of the mineral *wollastonite*. Combined with the silicates of other metals, calcium silicates are widely distributed. They can be prepared by fusing lime and silica (sand) together. They derive their chief interest from the fact that they are important constituents of cement and glass.

**Calcium oxalate ( $\text{CaC}_2\text{O}_4$ ).** This compound owes its chief interest to the fact that it is one of the most insoluble of the compounds of calcium. When a soluble oxalate, such as ammonium oxalate  $((\text{NH}_4)_2\text{C}_2\text{O}_4)$ , is added to a neutral solution of any calcium compound, calcium oxalate precipitates as a fine white powder. A solution of ammonium oxalate is therefore used as a reagent for the detection and estimation of calcium.

## STRONTIUM

**Occurrence and preparation.** Although somewhat widely distributed, strontium is the least abundant of the alkaline earth metals. Its chief minerals are *celestite* ( $\text{SrSO}_4$ ) and *strontianite* ( $\text{SrCO}_3$ ). The former is the more abundant and is found especially on some of the islands in Lake Erie. At Put in Bay beautiful large crystals of the mineral are found, lining the walls of Strontia Cave.

The metal was first isolated by Davy (1807), although in an impure state. Its preparation is much more difficult than that of calcium, although the general methods involved are the same. It closely resembles calcium in its general properties.

**Compounds of strontium.** The largest deposits of strontium ores in the United States are in Arizona, California, and Texas. Our consumption of strontium compounds is very limited, and the supply is largely imported from England. The compounds of strontium are very similar to those of calcium and for this reason will be discussed very briefly.

**Strontium oxide ( $\text{SrO}$ ); strontium hydroxide ( $\text{Sr(OH)}_2$ ).** The oxide is obtained by heating the carbonate. It combines with water to form the hydroxide, which is a moderately strong base. The latter is fairly soluble in hot water and crystallizes from the solution in the form of the octahydrate  $\text{Sr(OH)}_2 \cdot 8 \text{H}_2\text{O}$ . The hydroxide forms with sucrose an insoluble compound which can easily be decomposed into its original components. It was formerly used in the United States for the refining of sugar, to extract the sugar from uncrystallizable sirups, and is still used for this purpose in European countries.

**Strontium nitrate ( $\text{Sr(NO}_3)_2$ ).** This salt separates from a hot aqueous solution in the anhydrous form, while from a cold solution it separates as a tetrahydrate  $\text{Sr(NO}_3)_2 \cdot 4 \text{H}_2\text{O}$ . When ignited with combustible materials it imparts a brilliant crimson color to the flame and is therefore used in the manufacture of red lights. It is also used in making flares and signal shell and lights.

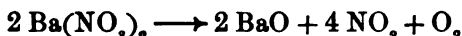
**Other compounds of strontium.** Among the other compounds of strontium the following may be mentioned: *strontium chloride* ( $\text{SrCl}_2 \cdot 6 \text{H}_2\text{O}$ ), *strontium bromide* ( $\text{SrBr}_2$ ), and *strontium iodide* ( $\text{SrI}_2$ ), which are all white solids, very soluble in water; *strontium sulfide* ( $\text{SrS}$ ), which is even more phosphorescent than calcium sulfide under the same conditions; and *strontium carbonate* ( $\text{SrCO}_3$ ), prepared from the chloride or nitrate by precipitation with ammonium carbonate. A number of compounds of strontium are used in medicine.

### BARIUM

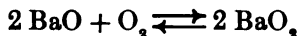
**Occurrence and preparation.** Like strontium and calcium, barium is widely distributed as a constituent of igneous rocks. Its most abundant forms are *barite* ( $\text{BaSO}_4$ ) and *witherite* ( $\text{BaCO}_3$ ). The former is the more abundant and is mined in considerable quantities, especially in Missouri, for use as a paint pigment. The statements made in reference to the preparation and properties of strontium apply equally to barium.

**Compounds of barium.** The compounds of barium are very similar to those of calcium and strontium. They are prepared either directly or indirectly from barite. This is first converted into the sulfide or carbonate, and from these the chloride and nitrate are prepared by the action of the appropriate acids. The soluble compounds of barium are poisonous.

**Barium oxide ( $\text{BaO}$ ); barium peroxide ( $\text{BaO}_2$ ).** Barium oxide is prepared by heating the nitrate rather than the carbonate, since the latter is decomposed only with great difficulty:



Heated to a low red heat in the air, barium oxide combines with oxygen, forming the peroxide  $\text{BaO}_2$ :



This reaction is reversible, and it will be recalled that it serves as a possible method for separating oxygen from the air (p. 21).

Barium peroxide is a white solid, insoluble in water. It combines with water to form the hydrate  $\text{BaO}_2 \cdot 10 \text{H}_2\text{O}$ . When

treated with acids it yields hydrogen peroxide (p. 86) and serves for the commercial preparation of this important compound. Strontium and calcium form similar peroxides, but they are not so readily obtained.

**Barium hydroxide ( $\text{Ba}(\text{OH})_2$ ).** Barium oxide resembles the oxides of calcium and strontium in that it readily combines with water to form the corresponding hydroxide. The hydroxide forms a number of hydrates, the most common one being the octahydrate  $\text{Ba}(\text{OH})_2 \cdot 8 \text{H}_2\text{O}$ , which crystallizes from solutions at ordinary temperatures. It is much more soluble than either calcium or strontium hydroxide, and its solution is often used as a reagent for detecting carbon dioxide, since it forms with it the difficultly soluble barium carbonate (p. 147). Its aqueous solution acts as a strong base.

**Barium chloride ( $\text{BaCl}_2$ ).** This salt is prepared by the action of hydrochloric acid upon barium carbonate or sulfide. It is quite soluble in water and crystallizes from saturated solutions in the form of white crystals, which have the formula  $\text{BaCl}_2 \cdot 2 \text{H}_2\text{O}$ . It is used as a reagent for the detection of sulfuric acid or a soluble sulfate, forming with them the insoluble barium sulfate (p. 321).

**Barium sulfate ( $\text{BaSO}_4$ ).** This compound has been known for a long time and is by far the most widely used of the compounds of barium. The native barium sulfate is a heavy mineral; hence the name *barite*, meaning "heavy," from which name that of the metal itself was derived. Our supply comes mainly from Georgia, Missouri, and Tennessee. With the exception of the sulfate of the rare element radium, it is the least soluble of all the sulfates. It is precipitated, even in the presence of strong acids, when a solution of a sulfate (or sulfuric acid) is added to a solution of a barium salt (p. 525). The native sulfate, as well as that prepared by precipitation, is used in large quantities as a pigment.

**Other compounds of barium.** *Barium carbonate* ( $\text{BaCO}_3$ ) is sometimes mixed with clay in the manufacture of terra-cotta ware. *Barium nitrate* ( $\text{Ba}(\text{NO}_3)_2$ ) is an oxidizing agent, and combustible materials mixed with it burn with a green flame. It

is therefore used in the manufacture of green lights. *Barium sulfide* ( $\text{BaS}$ ) resembles the sulfides of calcium and strontium in that it is phosphorescent and hydrolyzes with water, forming the hydroxide and acid sulfide. *Barium chromate* ( $\text{BaCrO}_4$ ) is a yellow solid, insoluble in water.

### QUESTIONS

1. Contrast the alkali metals and alkaline earth metals as to (a) valence, (b) method of preparation, (c) density, (d) action on water, and (e) solubility of compounds.

2. Give a simple method for distinguishing between the following compounds: potassium carbonate and calcium carbonate; fluorite and gypsum; strontium nitrate and sodium nitrate; calcite and celestite.

3. How could you prepare ammonium nitrate from air and hydrogen?

4. Does nitrogen fixation ever take place in the soil?

5. Would air-slaked lime serve to neutralize the acid in an acid soil?

6. Why do calcium and magnesium salts make a water hard while sodium salts do not?

7. Write the equations for preparing barium chloride from barium sulfate; strontium iodide from strontianite.

8. What is the deposit formed when certain hard waters are boiled?

9. Why will an air draft maintained in a limekiln lower the temperature required for producing lime?

### PROBLEMS

1. What weight of limestone containing 90 per cent calcium carbonate is required to make 10 tons of hydrated lime?

2. What weight of gypsum is required for the manufacture of 1000 kg. of plaster of Paris?

3. A certain city uses 10,000,000 gal. of water daily. 100 gal. of the water contains 120 g. of calcium acid carbonate and 30 g. of calcium sulfate. What weights of calcium hydroxide and sodium carbonate are required to soften the daily supply?

4. A paper factory requires 1000 kg. of calcium bisulfite daily. Calculate the weights of raw materials required for its preparation.

## CHAPTER XXXV

### THE MAGNESIUM FAMILY

	ATOMIC WEIGHT	DENSITY	MELTING POINT	BOILING POINT	OXIDE
Glucinum (Gl) . . . . .	9.10	1.93	1280.0°		GlO
Magnesium (Mg) . . . . .	24.32	1.74	651.0°	920°	MgO
Zinc (Zn) . . . . .	65.37	7.10	419.4°	950°	ZnO
Cadmium (Cd) . . . . .	112.40	8.64	320.9°	778°	CdO

**The family.** In the magnesium family are included the five elements, glucinum, magnesium, zinc, cadmium, and mercury. Among the first four of these metals there is a close family resemblance, such as has been traced between the members of the two preceding families. Mercury will be described in connection with copper, since in some respects it is more like that metal than it is like the members of the magnesium family.

### MAGNESIUM

**Occurrence.** Magnesium is a very abundant element in nature, ranking a little below calcium in this respect. It never occurs in an uncombined condition, but its compounds are common constituents of rocks and are found in sea water and mineral waters, being closely associated with the compounds of calcium. The element is also widely distributed throughout the animal and vegetable kingdoms. In the form of a definite mineral it occurs as *magnesite* ( $\text{MgCO}_3$ ) and *dolomite* ( $\text{CaCO}_3 \cdot \text{MgCO}_3$ ) and is usually a constituent of limestones. Among its silicates the following may be mentioned: *asbestos* ( $\text{CaMg}_3(\text{SiO}_3)_4$ ), in some forms of which the magnesium is partly replaced by iron; *talc*

( $\text{Mg}_3\text{H}_2(\text{SiO}_3)_4$ ); *serpentine* ( $\text{Mg}_3\text{Si}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ ); *meerschaum* ( $\text{Mg}_3\text{H}_4\text{Si}_2\text{O}_{10}$ ). Its presence in the Stassfurt salts has already been noted (p. 542). A small percentage is always present in chlorophyll, thus suggesting that it plays some part in the growth of the plant.

**The element.** Magnesium was first isolated in 1807 by Davy, who obtained it by the same methods which were successful in the isolation of the alkali and alkaline earth metals. Like most metals whose oxides are difficult to reduce with carbon, it was formerly prepared by heating its anhydrous chloride with sodium:



At present it is prepared by the electrolysis of anhydrous carnallite or chloride. The salt is melted in an iron pot which serves as the cathode, while the anode is a carbon rod dipping into the liquid.

Magnesium is a silvery white metal. Its density is 1.74, its melting point  $651^\circ$ , and its boiling point  $920^\circ$ . Air does not act rapidly upon it, but a thin film of oxide forms upon its surface, dimming its bright luster. It combines directly with most of the nonmetals, even with nitrogen; hence its use by Ramsay in the isolation of argon (p. 156). It is a strong reducing agent. When heated in the air it is easily ignited and burns with a brilliant white light, forming the oxide, together with a small percentage of the nitride. This light is very rich in the rays which affect a photographic plate, so that the powdered metal, either alone or mixed with potassium chlorate, is used as a source of artificial light in photography, as well as in pyrotechnics. It was especially adapted for making flares used during the World War for lighting up the battlefields. It is also used in the manufacture of *magnalium*, a light alloy of magnesium and aluminium having a high tensile strength.

**Compounds of magnesium.** The preparation of the compounds of magnesium presents no new problems. The carbonate found in nature is readily converted into other compounds by the

action of acids. Moreover, magnesium chloride is obtained as a by-product, especially in the preparation of potassium chloride (p. 543), and since this is very soluble, it serves as a material for the preparation of the insoluble salts.

**Magnesium oxide ( $MgO$ ); magnesium hydroxide ( $Mg(OH)_2$ ).** Magnesium oxide can be prepared by any of the general methods for preparing oxides. Commercially it is obtained by heating the carbonate, which is even more readily decomposed than calcium carbonate. It is a white powder, very soft and light, and is often known commercially as *magnesia* or *magnesia usta*. It resembles calcium oxide in many respects, but is even more infusible, although it can be melted in the electric furnace. With water it forms the hydroxide, but the combination takes place much more slowly, and with the production of less heat, than in the case of calcium oxide. Because of its highly infusible character it is used in the manufacture of fire brick, as a lining for furnaces, and for other purposes where a highly refractory substance is needed.

Magnesium hydroxide is an amorphous substance and is but slightly soluble in water. When heated it is easily decomposed into the oxide and water. Magnesium salts, as a rule, have no injurious effect upon the system, and for this reason either magnesium oxide or hydroxide serves as a very suitable antidote for poisoning by strong acids, for, since they are basic, they neutralize the acid, and neither the excess taken nor the salt formed causes injury.

**Precipitation of magnesium hydroxide.** Magnesium hydroxide, being insoluble, is precipitated when a solution of sodium or potassium hydroxide is added to a solution of a magnesium salt. With ammonium hydroxide, however, only a portion of the magnesium is precipitated. This is due to the fact that ammonium hydroxide is only slightly ionized, and in the presence of the ammonium salts formed in the reaction the extent of this ionization becomes still less, because of the influence of the ammonium ions present in the solution. As a result the concentration of the hydroxyl ions becomes so small that the solubility product of magnesium hydroxide is no longer exceeded.

**Magnesium chloride ( $\text{MgCl}_2$ ).** This compound is found in many natural waters and salt deposits and is obtained as a by-product in the manufacture of potassium chloride from carnallite. Under ordinary conditions it crystallizes from solutions as the hexahydrate  $\text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$ , although a number of other hydrates are known. When the hydrate is heated, magnesium oxide is formed:



Owing to the abundance of magnesium chloride, attempts have been made to utilize this reaction in the preparation of both magnesium oxide and hydrochloric acid.

The anhydrous magnesium chloride may be obtained by first preparing the double salt  $\text{NH}_4\text{Cl} \cdot \text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$  and then carefully heating it. The water of crystallization is expelled first, and afterwards, at higher temperature, the ammonium chloride volatilizes, leaving the anhydrous magnesium chloride.

Magnesium also forms oxychlorides which are coming into use especially for making floors and terra cotta. A common floor covering is made by adding magnesium chloride to a mixture of fiber (wood or asbestos) and magnesium oxide. With the proper amount of water the materials set, owing to the formation of the oxychloride  $3 \text{MgO} \cdot \text{MgCl}_2 \cdot 10 \text{H}_2\text{O}$ .

**Magnesium carbonates.** The normal carbonate  $\text{MgCO}_3$  occurs in nature as *magnesite* and, combined with calcium carbonate, as *dolomite* ( $\text{CaCO}_3 \cdot \text{MgCO}_3$ ). The normal salt is very similar to calcium carbonate in its properties, but is slightly more soluble in water and much more readily decomposed by heat. It is quite soluble in water containing carbon dioxide, owing to the formation of the soluble acid carbonate  $\text{Mg}(\text{HCO}_3)_2$ . When a solution of magnesium salt is precipitated with sodium or potassium carbonate, a white solid is obtained which is not the normal carbonate that one would naturally expect but a basic salt, the exact composition of which varies with the conditions of the experiment. As ordinarily prepared its composition is

expressed by the formula  $3 \text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 3 \text{H}_2\text{O}$ . This basic salt is known as *magnesia alba* and is used in medicine and as a cosmetic. Magnesite is mined in California and Washington and used for refractory purposes. The cheaper dolomite is gradually replacing it for such uses, especially as a lining for various furnaces.

**Magnesium sulfate ( $\text{MgSO}_4$ ).** Like the chloride, this salt is found in many salt beds, and deposits of the nearly pure compound occur in Wyoming and Washington. A number of hydrates are known. The monohydrate occurs in the Stassfurt deposits as *kieserite*, but the most common form is the heptahydrate  $\text{MgSO}_4 \cdot 7 \text{H}_2\text{O}$ , known as *Epsom salt*. This form is obtained by crystallizing magnesium sulfate from solution at ordinary temperature, and, unlike *kieserite*, it is very soluble in water. All the hydrates yield the anhydrous salt when heated to  $200^\circ$ , and this in turn decomposes at a white heat, leaving a residue of magnesium oxide.

Magnesium sulfate has many uses in the industries. It is used as a coating for cotton cloth, in the dyeing industry, in tanning, in the manufacture of paints and laundry soaps, to a limited extent in the preparation of sodium and potassium sulfates, and in medicine.

Magnesium sulfate was the first magnesium compound to be described. In 1695 Grew, a London physician, called attention to its occurrence in the waters of the famous spring located at Epsom, England; hence the name *Epsom salt*. It soon came into general use as a medicinal agent.

**Boiler scale.** When water which contains certain salts in solution is evaporated in steam boilers, a hard, insoluble material, called *scale*, deposits in the boiler. The formation of this scale may be due to several causes.

1. *To the deposit of calcium sulfate.* When a saturated solution of calcium sulfate is boiled, a little of the hydrated salt is precipitated. Superheating in a steam boiler, however, almost completely precipitates it as the anhydrous salt in the form of a hard scale.

2. *To decomposition of acid carbonates.* As we have seen, the acid carbonates of calcium and magnesium are decomposed on heating, forming insoluble normal carbonates:



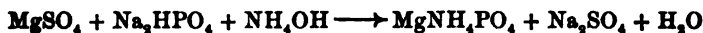
3. *To hydrolysis of magnesium salts.* Magnesium chloride and to some extent magnesium sulfate undergo hydrolysis when superheated in solution, and the magnesium hydroxide, being sparingly soluble, precipitates:



This scale adheres tightly to the boiler in compact layers and, being a nonconductor of heat, causes much waste of fuel. It is very difficult to remove, owing to its hardness and resistance to reagents. Thick scale sometimes cracks, and the water, coming in contact with the overheated iron, may cause an explosion. Moreover, the acids set free in the hydrolysis of the magnesium salts attack the iron tubes and rapidly corrode them. These causes combine to make the formation of scale a matter which causes much trouble in cases where hard water is used in steam boilers. Water containing such salts should be softened, therefore, before being used in boilers.

**Magnesium silicates.** Many silicates containing magnesium are known, and some of them are important substances. *Serpentine*, *asbestos*, *talc* (or *soapstone*), and *meerschaum* are examples of such substances. Asbestos is soft and fibrous and a nonconductor of heat and of electricity. It is used for fireproof material in a great variety of forms, such as cloth, paper, board, and rope. It is also used as a covering for pipes, furnaces, and boilers, to diminish heat radiation. It also has many uses as an insulator in electrical devices. The chief source of asbestos is the province of Quebec, Canada. Soapstone is a valuable material for making sinks and table tops. It is sometimes called *French chalk*. Meerschaum is used for pipe bowls and similar articles.

**Other magnesium compounds.** *Magnesium sulfide* ( $\text{MgS}$ ) is prepared by heating a mixture of magnesium and sulfur. It is a yellowish-gray solid and resembles calcium sulfide in its action toward water. *Magnesium nitride* ( $\text{Mg}_3\text{N}_2$ ) is formed by the direct union of magnesium and nitrogen at high temperature. It reacts with water, forming magnesium hydroxide and ammonia. The *phosphates of magnesium* resemble those of calcium in their composition and general properties. When a solution of disodium phosphate is added to a solution of any magnesium compound containing ammonium hydroxide, magnesium ammonium phosphate is precipitated:



This crystallizes in the form of the hexahydrate, which is somewhat unstable. If filtered off and heated to redness, however, it is converted into magnesium pyrophosphate ( $\text{Mg}_2\text{P}_2\text{O}_7$ ), which is perfectly stable:



From the weight of the pyrophosphate it is possible to calculate the weight of magnesium present in the original solution. These reactions serve in the laboratory for the quantitative determination either of magnesium or of phosphoric acid.

## ZINC

**Occurrence and metallurgy.** Zinc does not occur free in nature. It is not a constituent of common rocks, and its occurrence is rather local and confined to deposits or pockets. Its chief ores are the following: *sphalerite* ( $\text{ZnS}$ ); *zincite* ( $\text{ZnO}$ ); *smithsonite* ( $\text{ZnCO}_3$ ); *willemite* ( $\text{Zn}_2\text{SiO}_4$ ); *calamine* ( $\text{Zn}_2\text{SiO}_4 \cdot \text{H}_2\text{O}$ ); *franklinite* ( $\text{ZnFe}_2\text{O}_4$ ). In the United States it occurs in a number of different localities but most abundantly in Missouri, Montana, and New Jersey.

In the metallurgy of zinc the ores are first converted into the oxide by roasting, and the oxide is then reduced with carbon.

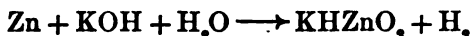
A mixture of zinc oxide and coal is heated in earthenware retorts. The zinc oxide is thereby reduced, and the resulting zinc, being volatile at the temperature of the retort, distills and is collected in suitable receivers. At first the zinc collects in the form of a powder known as *zinc dust*, which, however, contains some zinc oxide. Later, when the receiver has become hot, the zinc condenses to a liquid and is drawn off into molds. In this form it is impure and is known as *spelter*.

Commercial zinc ordinarily contains a number of impurities, especially carbon, arsenic, cadmium, and iron. These can be largely removed by distillation. Zinc containing less than 0.001 per cent of impurities has been obtained by electrolysis of a pure salt and subsequent distillation under diminished pressure.

**Properties.** Pure zinc is a bluish-white metal. Its density is 7.10, its melting point  $419.4^\circ$ , and its boiling point  $950^\circ$ . Some of its physical properties are greatly modified by the temperature and the previous treatment of the metal. When allowed to solidify from the liquid state, it is highly crystalline and is

quite hard and brittle. At temperatures between 100° and 150° it is malleable and can be rolled into thin sheets, which retain their softness and malleability at ordinary temperatures. Above 150° it again becomes very brittle. When melted and poured slowly into water, it forms thin, brittle flakes, and in this condition is called *granulated zinc*, or *mossy zinc*.

Zinc tarnishes superficially in moist air, owing to the formation of a basic carbonate. It does not decompose even boiling water, but at a high temperature it acts upon steam, forming the oxide and hydrogen. When heated sufficiently in oxygen or air it burns with a bluish flame. Dilute acids have but little action upon the pure metal, since the hydrogen at first liberated collects on the surface of the metal in the form of a thin film, and the action soon ceases. If another metal below zinc in the electrochemical series, such as iron, copper, or platinum, is present, either as an impurity or simply in contact with the zinc, the hydrogen escapes from the surface of the less positive metal, and the zinc rapidly dissolves. Zinc also dissolves in a hot solution of potassium hydroxide with liberation of hydrogen, the equation probably being:



**Uses of zinc.** The chief use of zinc is in the manufacture of *galvanized iron*. This is sheet iron covered with a thin layer of zinc, which protects the iron from the action of air and water. About two thirds of all the zinc produced is used in this way. Large quantities are also used in the manufacture of alloys (table, p. 642). The metal is also used in the construction of batteries and as a roofing material. In the laboratory it is used in the preparation of hydrogen and as a reducing agent.

**Compounds of zinc.** In general the compounds of zinc are similar in formula and appearance to those of magnesium. They often differ from them quite markedly, however, in chemical conduct. Either the metal, its oxide, or the natural carbonate or sulfide serves as a convenient material for the preparation of these compounds.

**Zinc oxide (zinc white) ( $\text{ZnO}$ ).** This is a white powder obtained by roasting the ores in a current of air or, in the pure state, by oxidizing the metal itself. It turns yellow when heated, but regains its white color on cooling. It is used very largely as a white pigment in paints, under the name of *zinc white*, and has an advantage over white lead in that it is not darkened by the sulfur compounds which are present in the air, especially in manufacturing districts. Large amounts are used annually in the manufacture of rubber goods, especially as a filler for automobile tires.

**Zinc hydroxide ( $\text{Zn(OH)}_2$ ).** This compound is precipitated in the form of a white solid when an alkali is added to a solution of a zinc salt. It is an amphoteric hydroxide, dissolving in both acids and alkalies. In solution it ionizes as follows:



**Soluble salts.** The soluble salts of zinc can be prepared by dissolving the metal or its oxide in the appropriate acid. The chloride and sulfate are the most familiar.

**Zinc chloride ( $\text{ZnCl}_2$ ).** This salt is readily soluble in water and in alcohol. It is strongly hydrolyzed in water, and upon evaporation the solution yields a basic chloride  $\text{ZnOHCl}$  in addition to zinc chloride. When fused and allowed to cool, it forms a hard mass which has a marked affinity for water and is strongly caustic. The largest use of zinc chloride is as wood preservative.

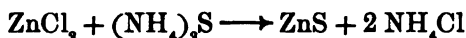
**Zinc sulfate ( $\text{ZnSO}_4$ ).** Under ordinary conditions this salt crystallizes from water in the form of a heptahydrate  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ , which has long been known under the name of *white vitriol*. Commercially the salt is prepared by roasting sphalerite. It is used in medicine, and to a limited extent in the dyeing and printing of cloth.

**Insoluble salts.** These are prepared by the ordinary methods of precipitation. The most important ones are the sulfide and carbonate. The normal carbonate  $\text{ZnCO}_3$  is precipitated upon

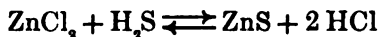
the addition of sodium bicarbonate to a solution of a zinc salt. Normal sodium carbonate precipitates basic salts, as in the case of magnesium.

**Zinc sulfide (ZnS).** The natural zinc sulfide (sphalerite, blende, or blackjack) varies, largely according to the impurities present, from a light-yellow, transparent, resinous solid to a black mass. As prepared in the laboratory by precipitation, it is a white solid. The fact that zinc is the only one of the common metals that forms a *white* sulfide is of importance in chemical analysis.

**Formation of zinc sulfide by precipitation.** Zinc sulfide is nearly insoluble in water and is formed as a precipitate when ammonium sulfide is added to a solution of a salt of zinc:



On the other hand, when hydrogen sulfide is passed into such a solution, the precipitation of the zinc sulfide soon ceases, an equilibrium resulting, as expressed in the following equation:



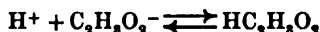
In accordance with the theory of precipitation (p. 523) this equilibrium results in the following way: While zinc sulfide is commonly said to be insoluble, because it is nearly so, it really has a very perceptible solubility. Before it can begin to precipitate, the concentration of the zinc ions and sulfur ions must be large enough to exceed the solubility product of the zinc sulfide, as expressed in the following equation:

$$[\text{Con. Zn}^{++}] \times [\text{Con. S}^{--}] > K$$

There is an abundant concentration of the zinc ions supplied by the zinc salt; moreover, at the beginning of the reaction the concentration of the sulfur ions derived from the hydrogen sulfide is fairly large, so that the solubility product, *K*, of zinc sulfide is exceeded and precipitation takes place. As the reaction proceeds, however, increasing quantities of hydrogen chloride are formed, and the hydrogen ions derived from this compound diminish the extent of the ionization of the hydrogen sulfide. The concentration of the sulfur ions, therefore, rapidly decreases until the solubility product of the zinc sulfide is no longer exceeded and precipitation ceases.

It is interesting to note, however, that if a normal salt of some weak acid, such as sodium acetate ( $\text{NaC}_2\text{H}_3\text{O}_2$ ), is added to the solution of the zinc salt, and the hydrogen sulfide then passed in, the precipitation of the zinc

sulfide continues to completion, for as fast as the hydrogen ions are formed in the reaction, they enter into an equilibrium with the anion of the weak acid, as shown in the following equation :



This keeps the concentration of the hydrogen ions too low to have any marked effect upon the concentration of the sulfur ions, so that precipitation continues to completion. It may be added that the addition of sodium acetate to an acid solution is a device often employed when it is desired to reduce the concentration of the hydrogen ions to a minimum value and yet have the solution distinctly acid in reaction.

### CADMIUM

**Preparation, properties, and uses.** This metal is associated with zinc in nature, small quantities occurring in many zinc ores in about the ratio of 1 part of cadmium to 200 parts of zinc. In the course of the metallurgy of zinc the cadmium compounds are changed to cadmium oxide, which is then reduced by carbon, the cadmium distilling over with the zinc. Being more volatile than the zinc, it is largely concentrated in the first portions of the distillate. From these portions the pure metal can be obtained by fractional distillation. The metal resembles zinc in appearance. Its density is 8.64, its melting point  $320.9^\circ$ , and its boiling point  $778^\circ$ . The principal use of the metal is in the manufacture of low-melting alloys employed in automatic fire extinguishers.

Only small quantities of cadmium are produced, since there is little demand for it at present prices. The zinc spelter obtained from the ore of the western states contains about 0.4 per cent of cadmium. Although its presence in the zinc is undesirable, yet under present conditions it is not economical to separate it.

**Compounds of cadmium.** Some of the most important of the compounds of cadmium are the following: *Cadmium oxide* ( $\text{CdO}$ ) is obtained by heating cadmium in air or oxygen. It is a brown powder and combines with water to form *cadmium hydroxide* ( $\text{Cd}(\text{OH})_2$ ), a white, insoluble solid. *Cadmium chloride* ( $\text{CdCl}_2$ ) crystallizes from water as the dihydrate. *Cadmium bromide* ( $\text{CdBr}_2$ ) and *cadmium iodide* ( $\text{CdI}_2$ ) resemble the chloride and

are used to some extent in photography. *Cadmium sulfate* crystallizes from water as a hydrate of the formula  $3 \text{ CdSO}_4 \cdot 8 \text{ H}_2\text{O}$ , while under similar conditions *cadmium nitrate* forms the hydrate  $\text{Cd}(\text{NO}_3)_2 \cdot 4 \text{ H}_2\text{O}$ . *Cadmium sulfide* ( $\text{CdS}$ ) is commercially the most important of the cadmium compounds. It occurs in nature in the form of the mineral known as *greenockite*. In the laboratory it is prepared by passing hydrogen sulfide into a solution of a cadmium salt. It is bright yellow in color and is used as a pigment. Its largest use is in making colored glass.

### GLUCINUM

**Preparation and properties.** Glucinum, known also as beryllium, since it was first found in the mineral *beryl*, is a rather rare metal. In 1828 Wöhler first isolated it by heating the chloride with potassium. It is a hard metal and has a bright, metallic luster. When prepared by electrolysis, crystals are obtained which have a density of 1.93. It is similar to the other metals of the family in its behavior toward air and acids. It resembles zinc in that it readily dissolves in alkalis. The metal is very difficult to prepare; indeed, there is some question as to whether it has ever been obtained in a pure state.

**Compounds of glucinum.** This element forms a series of compounds resembling in formulas the corresponding compounds of the other members of the magnesium family. The hydroxide  $\text{Gl}(\text{OH})_2$ , like zinc hydroxide, is insoluble in water but dissolves in both acids and alkalis. The salts of glucinum readily hydrolyze and form basic compounds. The soluble compounds of the element have a sweetish taste, which fact suggested the name *glucinum*, from the Greek word meaning "sweet."

### QUESTIONS

1. In what respects do the members of the magnesium family resemble the alkali metals and the alkaline earth metals?
2. What are the relative advantages of the following bases: sodium hydroxide, calcium hydroxide, and magnesium hydroxide?
3. How could water containing magnesium bicarbonate be softened?
4. How could you prepare magnesium chloride from magnesium sulfate?
5. Name the compounds so far studied that are derived from the Stassfurt salts.

6. (a) How could you distinguish between zinc oxide and magnesium oxide? (b) between Glauber's salt and Epsom salt?

7. Show by equations how the following compounds of zinc could be prepared from the metal itself: the oxide, chloride, sulfate, carbonate, hydroxide, nitrate, and sulfide.

### PROBLEMS

1. What weight of carnallite is required for the preparation of 100 kg. of magnesium, assuming that 90 per cent of the magnesium present in the carnallite can be isolated?

2. What are the relative proportions of calcium carbonate and magnesium carbonate in dolomite?

3. What weight of magnesite, 95 per cent pure, is required for the preparation of 100 kg. of Epsom salt?

4. One gram of a rock containing magnesium carbonate was dissolved in acid and after appropriate treatment the magnesium present was precipitated by disodium phosphate in the presence of ammonium hydroxide. The precipitate when dried and heated to redness gave 0.45 g. of magnesium pyrophosphate. Calculate the percentage of magnesium carbonate in the rock.

5. What weight of zinc will 100 tons of franklinite yield?

6. One gram of a zinc ore was dissolved and the zinc present precipitated by hydrogen sulfide. The resulting zinc sulfide weighed 0.41 g. Calculate the percentage of zinc in the ore.

7. The number representing the weight of any given amount of magnesium pyrophosphate must be multiplied by what factor to obtain the weight of magnesium present?

## CHAPTER XXXVI

### THE ALUMINIUM GROUP

**The group.** With the exception of aluminium, none of the elements of Group III of the periodic table are well known or abundant. Boron has already been considered, and the others fall naturally into two families. The one includes aluminium, together with gallium, indium, and thallium; the other, scandium and yttrium, together with a large group of elements whose oxides are collectively called the *rare earths*.

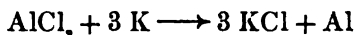
All of the elements of this group are tervalent in their compounds, though some of the rarer elements, particularly thallium, have lower valences as well. With few exceptions their salts are colorless, save when they are derived from a colored acid. The bases which these elements form are nearly all weak, and many of their salts are somewhat hydrolyzed in solution. A brief mention of the rarer elements will be made after aluminium has been considered.

### ALUMINIUM

**Occurrence.** Next to oxygen and silicon, aluminium is the most abundant of all the elements. The free element is not found in nature, but its compounds, especially the silicates, are abundant and widely distributed, being essential constituents of all important soils and rocks excepting limestone and sandstone. The *feldspars*, which are the most abundant of all the minerals in the earth's crust, are all silicates of aluminium and either sodium, potassium, or calcium. Since the soil has been formed largely by the disintegration of these rocks, it is rich in the silicates of aluminium, chiefly in the form of clay. Some of

the other forms in which aluminium occurs in nature are the following: *corundum* ( $\text{Al}_2\text{O}_3$ ); *emery* ( $\text{Al}_2\text{O}_3$  colored black with oxide of iron); *cryolite* ( $\text{Na}_3\text{AlF}_6$ ); *bauxite*, a mixture of iron oxide and hydrated aluminium oxides ( $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$  and  $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ ). Bauxite is the ore from which aluminium is prepared. Nearly all the bauxite used in the United States comes from Arkansas; a limited amount is imported from South America.

**Preparation.** Aluminium was first prepared by Wöhler in 1827 by heating anhydrous aluminium chloride with potassium:



Although the metal is very abundant in nature, and possesses many desirable properties, the cost of separating it from its ores by the earlier methods was so great that it remained almost a curiosity until comparatively recent years, when greatly improved methods of preparation came into use. It is now prepared by the electrolysis of aluminium oxide ( $\text{Al}_2\text{O}_3$ ) dissolved in melted cryolite—a method first patented by the American chemist Hall in 1886.

**The commercial preparation of aluminium.** The process is carried out in carbon-lined pots (Fig. 163), into which project carbon blocks. The apparatus is connected with an electrical generator in such a way that the carbon lining serves as the cathode and the carbon blocks serve as the anode. Each pot is partially filled with cryolite and the current is turned on, generating sufficient heat to melt the cryolite. Aluminium oxide is then added, and dissolves in the liquid cryolite to form an electrolyte. Upon electrolysis it yields aluminium and oxygen. The temperature is maintained above the melting point of aluminium, and the liquid metal, being heavier than cryolite, sinks to the bottom of the vessel, from which it is tapped off from time to time through the tap hole *C*. The oxygen in part escapes as gas, and in part combines with the carbon of the anode.

The largest expense in the process, apart from the cost of electrical energy, is the preparation of aluminium oxide free from other oxides, for most of the oxide found in nature is too impure to serve without refining. Bauxite is used as the ore, because it is converted into pure oxide without great difficulty. The iron oxide, which is the chief impurity, is separated by treatment of the ore with sodium hydroxide. Since common clay is a silicate of aluminium and is everywhere abundant, it might be expected

that this would be utilized in the preparation of aluminium. It is, however, very difficult to extract the aluminium from a silicate, and no practical method has been found which will accomplish this.

As a result of the introduction of the electrolytic method for preparing aluminium, the production of the metal increased from 83 lb. in 1883 to 225,000,000 lb. in 1918, while the price decreased from \$5 to about 80 cents

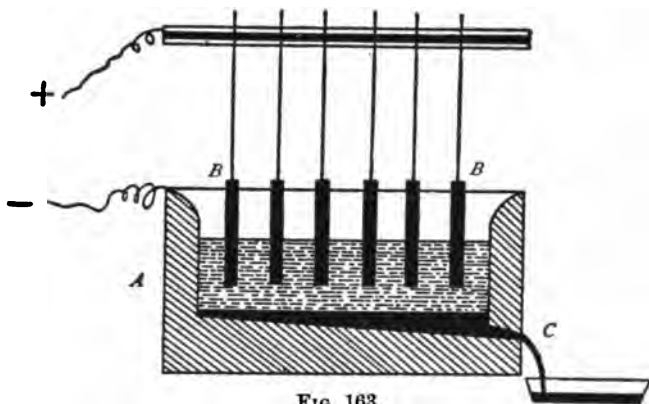


FIG. 163

per pound. During the World War, production was at a maximum, since the metal has many war uses. Aluminium stands fifth in the world's production of metals (the order being iron, copper, zinc, lead, aluminium), and the United States produces about half of it.

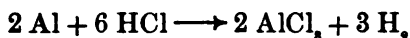
**Properties.** Aluminium resembles tin in appearance. Its density is 2.65, being only about one third that of iron. It melts at  $658.7^{\circ}$ . It is ductile and malleable, especially at temperatures between  $100^{\circ}$  and  $150^{\circ}$ , when it can be hammered into very thin sheets. At higher temperatures, near its melting point, it is very brittle. It is fairly hard and strong, being superior to most metals in these respects, although not equal to steel. It is an excellent conductor of heat and electricity.

Aluminium is but slightly acted upon by water, while moist air merely dims its luster. Further action is prevented in each case by the formation of a very thin film of oxide upon the surface of the metal. It combines with many of the nonmetals, especially with the halogens and the members of the sulfur

family. It is an excellent reducing agent, combining with oxygen at high temperatures, with liberation of much heat:



Nitric acid and dilute sulfuric acid have but little action upon it; concentrated sulfuric acid dissolves it, forming the sulfate and liberating sulfur dioxide. Hydrochloric acid is its best solvent:



Aluminium resembles zinc in that it readily dissolves in strong alkalis, forming aluminates and liberating hydrogen. It is also acted upon by sodium chloride, especially in the presence of oxygen and dilute acids such as acetic acid.

**Uses.** The lightness and strength of aluminium, together with its inactivity toward air and water, suggest a variety of applications for the metal. About one third of the output of the metal is used in the automobile industry. In pure form, it is used for certain construction purposes and for the manufacture of cooking utensils. In the form of a fine powder suspended in a suitable liquid, it makes an efficient silver-like paint. Although not as good a conductor of electricity as copper for a given cross section of wire, nevertheless, weight for weight, it is an even better conductor and is used in electrical construction, especially for long-distance power wires. The pure metal is also used as a reducing agent in separating certain metals from their oxides and in the welding of iron (Goldschmidt process). It is used as a *deoxidizing agent* in the manufacture of iron and steel, since a small quantity added to molten steel combines with any oxygen remaining in the metal. A large number of alloys of aluminium have been prepared, and many of them are of the greatest importance. Its alloys with copper (aluminium bronze) as well as with copper and zinc are easily cast into form and are not acted upon by the air. *Duralumin* contains about 95 per cent aluminium and small amounts of copper, magnesium, and manganese. *Magnalium* (p. 573) is silver-white and very light in weight.

The World War developed many new uses; for example, about one third of the weight of the Liberty motor was composed of aluminium. It was also used in the construction of many parts of aeroplanes. The powdered metal was used in incendiary bombs and as a constituent of some explosives.

**Goldschmidt welding process.** The property possessed by aluminium of reducing oxides with the liberation of a large amount of heat is turned into practical account in the welding of metals. The German chemist Goldschmidt was the first to use aluminium for this purpose. The welding of metals by this method may be illustrated by a single example, namely, the welding of car rails — a process often carried out in connection with electric railways to secure good electrical connection. The ends of the rails are accurately aligned and thoroughly cleaned. A sand mold *A* (Fig. 164) is then clamped about the ends of the rails, leaving sufficient space so that the metal can flow in. The ends of the rails are heated to redness by the flame from a gasoline compressed-air torch directed into the opening in the mold. Just over the opening is placed the conical-shaped crucible *B*, which contains a mixture of iron, metallic oxides, and aluminium. When the ends of the rails have been heated to redness by the torch, the mixture in the crucible is ignited, and after a few seconds the crucible is opened at the bottom, and the molten metal resulting from the reaction in the crucible is allowed to flow into the mold. In this way the molten metal surrounds the ends of the rails and, as it cools, welds them firmly together. A mixture of the metallic oxides and aluminium ready for use in welding is sold under the name of *thermite*.

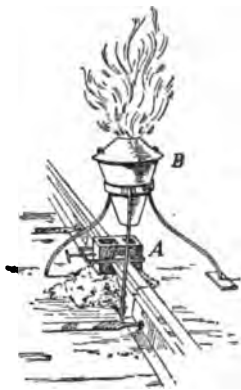
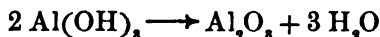


FIG. 164

**Compounds of aluminium.** Aluminium is a trivalent metal, and the formulas of its compounds therefore resemble those of bismuth and antimony. Aluminium hydroxide, like antimony hydroxide, is amphoteric. With strong bases it forms aluminates such as sodium aluminate ( $\text{NaAlO}_2$ ), derived from the partial anhydride  $\text{AlO} \cdot \text{OH}$ , while with acids it forms salts such as the chloride  $\text{AlCl}_3$  and the sulfate  $\text{Al}_2(\text{SO}_4)_3$ . These salts are characterized by their great tendency to undergo hydrolysis.

Aqueous solutions of the chloride and sulfate are strongly acid in reaction, while the carbonate and sulfide are completely decomposed by water (p. 329).

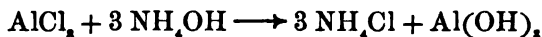
**Aluminium oxide ( $\text{Al}_2\text{O}_3$ ).** The occurrence of aluminium in nature in the form of *corundum* and *emery* has been mentioned already. In transparent crystals tinted different colors by traces of other substances, often in colloidal dispersion, it forms such precious stones as the *sapphire*, *ruby*, *oriental amethyst*, and *oriental topaz*. All of these are very hard, falling but little short of the diamond in this respect. The cheaper forms (corundum and emery) are used as abrasives. By igniting the hydroxide the pure aluminium oxide may be obtained in the form of a white, amorphous powder:



When heated to about  $1900^\circ$  it melts, and on cooling forms a crystalline mass resembling natural corundum. Some forms of laboratory apparatus, such as crucibles and tubes, are being made of aluminium oxide. When used for this purpose the oxide is known as *alundum*.

**Commercial preparation of gems.** A number of gems are now prepared in the laboratory from molten aluminium oxide. The white sapphires so extensively advertised are simply the pure oxide. By incorporating with the melted oxide small percentages of certain metallic oxides, different tints or colors are obtained, and in this way are prepared such gems as the ruby, the oriental amethyst, and the yellow and blue sapphires, which are practically identical in composition and properties with the natural stones.

**Aluminium hydroxide ( $\text{Al}(\text{OH})_3$ ); aluminic acid ( $\text{HAlO}_2$ ).** We should expect the insoluble aluminium hydroxide to be precipitated by the action of a soluble base on a salt of aluminium:



The white precipitate so obtained is usually given the formula  $\text{Al}(\text{OH})_3$ , but Weiser has shown that it is a typical colloidal gel consisting of the oxide in various stages of hydration. It is amphoteric in character, dissolving in acids to form aluminium salts such as  $\text{AlCl}_3$ , and in alkalis to form such salts as

$\text{NaAlO}_2$ , derived from the acid  $\text{HAlO}_2$  or  $\text{AlO} \cdot \text{OH}$ . This acid is called *aluminic acid*, and its salts *aluminates*. In a general way we may regard the gel as maintaining the equilibrium



since derivatives of the ions  $\text{Al}^{+++}$  and  $\text{AlO}_2^-$  may be secured from it by the addition of the appropriate reagent. When aluminium oxide is dissolved in alkali, and the solution is diluted until hydrolysis occurs, the hydroxide  $\text{Al}(\text{OH})_3$  is obtained in nearly constant composition.

A number of minerals, such as spinel ( $\text{Mg}(\text{AlO}_2)_2$ ), are found in nature which are salts of the acid  $\text{HAlO}_2$ .

**Spinel minerals.** A number of other trivalent hydroxides act in this same way, yielding salts analogous to spinel. Many of these are important minerals and are sometimes called collectively *the spinels*. A few of them are as follows:

Spinel . . . . .	$\text{Mg}(\text{AlO}_2)_2$ or $\text{MgO} \cdot \text{Al}_2\text{O}_3$
Franklinite . . . . .	$\text{Zn}(\text{FeO}_2)_2$ or $\text{ZnO} \cdot \text{Fe}_2\text{O}_3$
Magnetite . . . . .	$\text{Fe}(\text{FeO}_2)_2$ or $\text{FeO} \cdot \text{Fe}_2\text{O}_3$
Chromite . . . . .	$\text{Fe}(\text{CrO}_2)_2$ or $\text{FeO} \cdot \text{Cr}_2\text{O}_3$

**Use of aluminium hydroxide.** Aluminium hydroxide either combines with or adsorbs many soluble coloring substances, forming insoluble products. This property leads to its wide use in the dyeing industry. Many dyes will not adhere to natural fibers, such as cotton; that is, they will not dye fast. It is often possible to dye such cloth in the following way: The cloth is first soaked in a solution of an aluminium salt, such as the acetate, which readily undergoes hydrolysis. The cloth is then exposed to the action of steam, whereby the aluminium salt is completely hydrolyzed, the resulting aluminium hydroxide being thus thoroughly incorporated in the fiber. If the cloth is now dipped into a solution of the dye, the aluminium hydroxide fastens, or "fixes," the color substance upon the fiber by mutual precipitation or by selective adsorption (p. 511). A substance such as aluminium hydroxide which serves this purpose is known as a *mordant*, which means "biting," since it bites, or holds fast, the dye.

The value of aluminium hydroxide in the purification of water is due largely to its character as a positive colloid when freshly formed. When stirred through the water it slowly coagulates and in doing so carries with it any suspended matter present, including microorganisms. Any coloring matter present in the water is likewise adsorbed. Instead of adding the

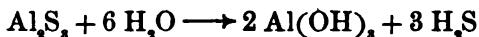
aluminium hydroxide itself to the water, it is much more efficient to produce it by precipitation. This is done by simply adding to the water some aluminium salt which readily hydrolyzes (the sulfate is generally used):



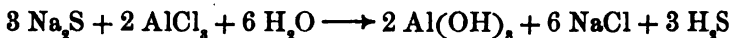
The sulfuric acid liberated reacts with the mineral matter in the water.

**Aluminium chloride ( $\text{AlCl}_3$ ).** This salt is prepared by passing dry chlorine or hydrogen chloride through a heated tube containing aluminium. It is a crystalline salt which sublimes without melting under atmospheric pressure and melts under increased pressure at  $193^\circ$ . It is strongly hygroscopic and fumes when exposed to the air, owing to the formation of hydrochloric acid through the action of moisture. The hexahydrate is formed by dissolving aluminium hydroxide in hydrochloric acid and evaporating to crystallization. When heated the hydrate is decomposed, forming aluminium oxide and water, so that the anhydrous salt cannot be prepared directly from the hydrate. The anhydrous salt is often used in certain organic reactions.

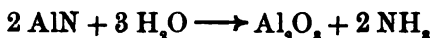
**Aluminium sulfide ( $\text{Al}_2\text{S}_3$ ).** The sulfide is prepared by heating a mixture of aluminium and sulfur to a high temperature. It may be obtained either as a black mass or as a yellow, crystalline solid. It is completely hydrolyzed upon the addition of water:



When a soluble sulfide, such as sodium or ammonium sulfide, is added to a solution of an aluminium salt, aluminium sulfide is probably formed, but it immediately hydrolyzes, so that the precipitate obtained consists of aluminium hydroxide. The complete reaction is represented by the following equation:



**Aluminium nitride ( $\text{AlN}$ ).** This compound is prepared by the direct union of aluminium and nitrogen at a high temperature. It derives its chief interest from the fact that, when it is treated with steam, ammonia is formed.



The nitrogen used in preparing the nitride is obtained from the air. It is possible, therefore, through the intermediate formation of aluminium nitride to convert the nitrogen from the air into ammonia (p. 566).

**Aluminium sulfate** ( $\text{Al}_2(\text{SO}_4)_3$ ). This compound is prepared commercially by the action of sulfuric acid upon either bauxite or kaolin, which is an abundant silicate of aluminium. The salt crystallizes from water in quite a variety of hydrates, the usual one having the composition expressed by the formula  $\text{Al}_2(\text{SO}_4)_3 \cdot 18 \text{H}_2\text{O}$ . It is the cheapest of the soluble salts of aluminium and is therefore the one most largely used when a salt of this metal is desired. Its principal uses are in the manufacture of alum and paper, in the purification of water, and as a mordant in dyeing.

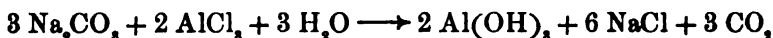
**The sizing of paper.** All paper intended for writing or printing must be *sized*, that is, coated over with some substance that will prevent the ink from spreading. Different methods have been devised for doing this, the following being a common one: The paper pulp is mixed with a soap made by heating resin with sodium hydroxide. A solution of aluminium sulfate is then added. This reacts with the soap to form sodium sulfate and aluminium resinate, the latter compound being largely hydrolyzed to resin and aluminium hydroxide. In this way the resin is thoroughly incorporated with the pulp. As the pulp is run over hot rolls in making the paper, the resin is melted, and on cooling forms a thin, impervious layer upon the surface of the paper.

**The alums.** If solutions of aluminium sulfate and potassium sulfate are mixed together and evaporated, well-formed octahedral crystals are deposited. These have the composition expressed by the formula  $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24 \text{H}_2\text{O}$ . This compound is a typical member of a class of compounds known as the *alums*. The composition of an alum is expressed by the general formula  $\text{M}'_2\text{SO}_4 \cdot \text{M}'''_2(\text{SO}_4)_3 \cdot 24 \text{H}_2\text{O}$ , or, more simply, as  $\text{M}'\text{M}'''(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$ , in which  $\text{M}'$  represents a univalent metal and  $\text{M}'''$  a trivalent metal. For the univalent metal one may have any of the alkali metals excepting lithium; also ammonium, silver, or thallium. For the trivalent metals, in

addition to aluminium, one may have iron or chromium, as well as a few of the other metals which can be obtained in a tervalent condition. Those alums that contain aluminium are white solids, those containing chromium have a ruby red or purple color, while those containing iron have a violet tint. They all crystallize readily, forming octahedral crystals which are isomorphous. Potassium alum ( $\text{KAl}(\text{SO}_4)_3 \cdot 12 \text{H}_2\text{O}$ ) and ammonium alum ( $\text{NH}_4\text{Al}(\text{SO}_4)_3 \cdot 12 \text{H}_2\text{O}$ ) are the most widely used.

Since the alums crystallize so readily, it is easy to obtain them in a pure condition. For this reason the aluminium alums have long been used in place of the much cheaper aluminium sulfate, which is difficult to purify. Improved methods have been devised for preparing this latter compound, so that now it is taking the place of alum for many commercial uses, such as the purification of water. The alums are used in the manufacture of paper, in water purification, and as mordants in dyeing. Smaller quantities are used in baking powders and in certain foods, such as pickles, since it makes them more crisp.

**Aluminium carbonate.** The normal carbonate of aluminium has not been prepared. One would naturally not expect it to be formed in the presence of water, for, being a salt of a very weak acid, as well as of a weak, insoluble base, it would be completely hydrolyzed. Accordingly, when a solution of a carbonate, such as sodium carbonate, is added to a solution of an aluminium salt, carbon dioxide is evolved and aluminium hydroxide, mixed with small percentages of basic carbonates, is precipitated. The main reaction takes place according to the following equation:



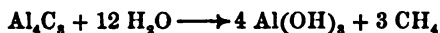
Because of this property alum is often used as a constituent of some varieties of baking powders.

**Alum baking powders.** These consist of a mixture of sodium bicarbonate, starch, and either an alum or a calcined mixture of sodium and aluminium sulfates. Formerly both the potassium and the ammonium alum were used, but they have been almost entirely superseded by the mixture just mentioned, as this is cheaper. Upon the addition of water to the baking powder a reaction slowly takes place, resulting in the formation

of aluminium hydroxide and carbon dioxide, the latter serving as the aerating agent. The starch absorbs moisture and thus, by preventing any reaction, causes the powder to retain its strength until used. The complete reaction taking place when water is added to a baking powder containing potassium alum is represented in the following equation :



**Aluminium carbide ( $\text{Al}_4\text{C}_3$ ).** This compound was obtained by Moissan by heating aluminium oxide with carbon in an electric furnace. Its chief interest lies in the fact that it reacts with water to form methane :



Since methane constitutes over 90 per cent of natural gas, it has been suggested that the latter product may, in some cases at least, have resulted from the action of water upon the carbides formed when the crust of the earth was in a molten condition.

**Aluminium silicates.** In discussing the occurrence of aluminium it was stated that the silicates of this metal are widely and abundantly distributed. Sometime in the history of the earth's formation its surface must have been composed of a solid igneous rock formed by the cooling of the molten mass. The various silicates of aluminium constitute by far the largest percentage of these igneous rocks. The most important of these are the *feldspars*, known as *orthoclase* ( $\text{KAlSi}_3\text{O}_8$ ), *albite* ( $\text{NaAlSi}_3\text{O}_8$ ), and *microcline*, which has the same chemical composition as orthoclase but is different in crystalline structure. The gradual disintegration, or weathering, of these rocks through various agencies, such as the action of air and water, has resulted in the formation of the mineral constituents of the soil. The changes taking place in the process are often very complex and are not well understood. Thus, in the weathering of orthoclase the potassium is removed, together with a portion of the silica, while at the same time water enters into chemical combination with the residue. In this way there is formed the soft, plastic mineral known as *kaolinite* ( $\text{Al}_2\text{Si}_2\text{O}_7 \cdot 2 \text{H}_2\text{O}$ , often written  $\text{Al}_2\text{O}_3 \cdot 2 \text{SiO}_2 \cdot 2 \text{H}_2\text{O}$ ). Large quantities of this mineral are sometimes found deposited in beds in fairly pure form. More

often it has been carried away by running water and mixed with various other products resulting from the crushing and weathering of rocks, especially silica (sand) and compounds of iron, calcium, and magnesium, in this way forming the product known as *clay*. *Kaolin* is a special kind of clay which usually burns white, so that it can be used for making chinaware. It is evident, therefore, that clay is extremely variable in composition, though the essential constituent appears to be kaolinite.

**Ultramarine.** The mineral known as *lapis lazuli* has long been known and highly prized because of its beautiful blue color. The powdered mineral was used by the ancients as a color pigment, called *ultramarine*. This term is now applied to the artificial product prepared by heating together, under suitable conditions, kaolin, charcoal, sodium carbonate, sodium sulfate, and sulfur. The product so obtained is very similar in composition and properties to the natural product and is much less expensive. By suitable variation of the method of preparation and of the ingredients employed, quite a variety of tints may be obtained. It is a very complex substance, and its exact composition is not known with certainty. Large quantities of it are used as a pigment, especially in wall papers.

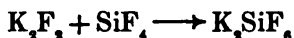
### DOUBLE AND COMPLEX SALTS

In the preceding pages a number of compounds have been represented as having formulas which indicate that they are made up of a combination of two different salts. Most of the Stassfurt minerals (p. 542) are of this kind; the formula of cryolite is often written  $3 \text{NaF} \cdot \text{AlF}_3$ ; the fluosilicates were formerly given such formulas as  $2 \text{KF} \cdot \text{SiF}_4$ ; finally, the alums present another group of the same general character. Among these salts two extreme cases can be defined.

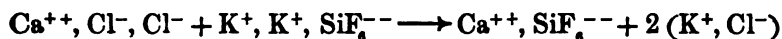
**Double salts.** Carnallite ( $\text{KCl} \cdot \text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$ ) is a good example of a *double salt*. When it is dissolved in water, the solution acts as though it contained a mixture of potassium and magnesium chlorides, both of which are freely ionized. Silver nitrate precipitates all the chlorine as silver chloride; ammonium phosphate precipitates the magnesium as magnesium ammonium phosphate ( $\text{MgNH}_4\text{PO}_4$ ). A salt of this kind, which in

solution *decomposes into its constituent salts and gives reactions for their individual ions, is called a double salt.* Most of the Stassfurt minerals belong to this class.

**Complex salts.** Potassium fluosilicate ( $K_2SiF_6$ ) may be taken as an example of a complex salt. It can be prepared by bringing together in solution the fluorides of potassium and silicon:

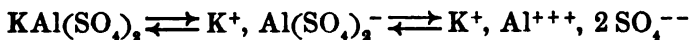


The product of the reaction cannot properly be regarded as a double salt, for it gives none of the reactions characteristic of the fluorides, from which it is formed. Thus, when calcium chloride is treated with potassium fluoride it precipitates insoluble calcium fluoride, while with fluosilicates it enters into double decomposition, as shown in the equation



The complex ion  $SiF_6^{--}$  acts as a radical in all of the reactions of the fluosilicates. This fact, together with the stability of the salts, has led chemists to regard the fluosilicates as salts of fluosilicic acid ( $H_2SiF_6$ ) rather than as made up of two different fluorides combined, as in the case of double salts. Compounds of this kind, *which yield ions other than those of the salts from which they may be formed, are called complex salts.*

**Intermediate types.** The two classes just described are extremes, and there is every gradation between them, the alums being an example of this intermediate class. In rather concentrated solution they in part dissociate into the constituent sulfates, which then give their individual ions. In part they act as complexes, giving the alkali metal as one ion and the remainder of the alum as the other. These transitions constitute an equilibrium which may be represented thus:



As the solution becomes more and more dilute the complex ion  $Al(SO_4)_2^-$  tends to dissociate more completely into its constituent ions, which are those of a simple salt.

## GALLIUM, INDIUM, AND THALLIUM

The other members of the aluminium family — gallium, indium, and thallium — are elements of rare occurrence in nature, and were discovered by spectroscopic study of various minerals. They have brilliant and characteristic spectrum lines, and through these are known to be widely distributed in certain classes of minerals; with the exception of a few rare ores of thallium, however, they have never been found to an extent of more than about 0.1 per cent in any mineral. All the metals are easily reduced from their oxides, resembling zinc and lead in this respect. Like aluminium, they are trivalent in their best-known compounds, but each of them forms at least one series of salts in which it is univalent or bivalent as well. As a trivalent metal each forms a number of alums.

**Gallium.** Gallium was discovered in certain zinc blende by the Frenchman Lecoq de Boisbaudran in 1875, and named in honor of his country, the Latin name for which is *Gallia*. It is found in ores of zinc, aluminium, and iron, the richest known source being the iron from the Cleveland district in England, which contains about 0.003 per cent of gallium. Traces of it are always present in bauxite. The largest amount of the metal produced in the United States was about 50 g. obtained as a by-product in a zinc smelter in Oklahoma. It is a shining white metal of very low melting point (30°). In addition to the usual series of salts, in which it is trivalent, it forms a second series in which it is bivalent.

**Indium.** This metal was discovered in a specimen of Freiburg zinc blende by Reich and Richter in 1863, while they were examining it spectroscopically for thallium. The name was suggested by its characteristic indigo-blue spectrum line. Its richest ores do not seem to contain above 0.1 per cent indium, and it is never found in appreciable quantities save in minerals containing zinc. It is a white metal, a little grayer than silver, and is as soft as wax. It melts at 155°, and its density is about 7.12. In addition to salts resembling those of aluminium it forms other series, in one of which it is bivalent and in the other univalent.

**Thallium.** Thallium is by far the most abundant of these three elements. It was discovered by Crookes in 1861 in the slimes from the lead chamber of a sulfuric acid factory. The name was suggested by its brilliant green spectrum line (*thallium* being derived from a Greek word meaning "a green twig"). It frequently accompanies the sulfides of the

heavier metals, such as copper, lead, iron, and zinc, and is obtained from the flue dusts which are formed in the roasting of such sulfides. To some extent it also accompanies potassium and has been found in carnallite. It is a heavy metal (density 11.9) and is softer than lead, which it very much resembles in appearance. It melts at 302°.

In its chemical conduct it is very interesting. As a trivalent element its salts resemble those of aluminium in a general way, though its hydroxide is rusty red in color, like ferric hydroxide, and its sulfide ( $Tl_2S_3$ ) is soluble in ammonium sulfide, like the sulfides of arsenic and antimony. As a univalent element it forms a hydroxide  $TlOH$ , which is a strong, soluble base like potassium hydroxide, and its salts are, as a rule, very similar to those of potassium. Its chloride and cyanide, however, are insoluble in water and acids, resembling the corresponding salts of silver in this respect.

### THE RARE EARTHS

**History.** In 1794 Gadolin discovered a new mineral, now called *gadolinite*, in the mines of Ytterby, near Stockholm, and found it to contain an oxide unlike any known at that time; this was named *yttria*. Within a few years other minerals were found which contained the same oxide, and since then a great many additional minerals have been added to the list. Almost at once yttria was recognized as a complex substance, and from that time to the present day many chemists have been engaged in determining its composition. In all, seventeen different elements are now clearly recognized to be present in yttria, and these are collectively called the *rare earth metals*. According to Moseley's work (p. 345) there is one of atomic number 61 as yet undiscovered. A list of these, together with their atomic weights, is as follows:

Scandium . . . . .	44.1	Terbium . . . . .	159.2
Yttrium . . . . .	89.0	Dysprosium . . . . .	162.5
Lanthanum . . . . .	139.0	Holmium . . . . .	163.5
Cerium . . . . .	140.25	Erbium . . . . .	167.7
Praseodymium . . . . .	140.6	Thulium . . . . .	168.5
Neodymium . . . . .	144.3	Neoytterbium . . . . .	172.0
Samarium . . . . .	150.4	Lutecium . . . . .	174.0
Europium . . . . .	152.0	Celtium . . . . .	(?)
Gadolinium . . . . .	157.3		

**Occurrence.** Minerals containing these elements have been found in many different countries including the United States. Some of these elements, for which delicate spectroscopic tests are known, are found to be widely distributed in many minerals, but in any appreciable quantities they are only of very local occurrence. As far as is known, no one of them ever occurs by itself, and a mineral which contains one is likely to contain most of them. One of these minerals, *monazite*, occurs largely in Brazil, India, and North Carolina, and usually contains from 1 to 8 per cent of thorium oxide, being the chief source of this rare and valuable substance. In extracting thorium large quantities of the rare earths accumulate, and the supply available for study is now unlimited.

**General characteristics.** A number of reactions are known which separate these elements as a group more or less completely from all others, but no one of the rare earths, with the exception of cerium, can be separated from the others by a single precipitation of the usual kind. Separations are only effected by fractional recrystallizations or precipitations repeated hundreds and often thousands of times, so that, with few exceptions, it is not certain that the compounds of any of these elements have been prepared in entirely pure form.

These elements are all trivalent, though cerium is often quadrivalent as well. In general they resemble aluminium, but their hydroxides are stronger bases, their salts are less hydrolyzed, and they form no alums. Most of their salts are colorless, though those of neodymium are pink, those of praseodymium green, and the ceric salts yellow or red.

**Relation to the periodic law.** In atomic weight these elements, with the exception of scandium and yttrium, form a continuous series extending from the weight 139 (La) to 174 (Lu), the first two in the list having much smaller weights. If they were arranged in the periodic table in the same way as other elements, they would evidently be distributed among all the different families. They are the most similar of all the elements, however, and are therefore placed in the position of a single element in the third group, with the frank admission that this introduces into the table an irregular and arbitrary feature which further study may make clear.

**Application.** A few practical applications have been found for some of these substances. By the electrolysis of a mixture of a number of their compounds an alloy of the metals is obtained, known as *mixed metal* (*mischmetall*). The heat of combustion of this alloy is greater than that of aluminium, and it is a more powerful reducing agent. It is therefore sometimes used in place of aluminium in the Goldschmidt process. An alloy of cerium with iron, known as *Auer metal*, produces brilliant sparks when drawn across a rough surface, and owing to this property it is used in the manufacture of gas-lighters and cigar-lighters. Cerium oxide is rather extensively used in the manufacture of arc-light electrodes. A small quantity (1 per cent) of cerium oxide is an essential constituent of gas mantles (p. 422), and some salts of cerium are used in medicine. Cerium oxide is a good catalytic agent in many reactions of oxidation, and it is also used in making glass for special purposes. Other applications are being sought, since at the present time many tons of rare earth material annually go to waste.

### QUESTIONS

1. What metals so far studied are prepared commercially by electrolysis?
2. What important discovery did Wöhler make in addition to the isolation of aluminium?
3. As a rule the solutions of sodium salts have a basic reaction while those of aluminium have an acid reaction. Explain.
4. Give the valences of the metals so far studied.
5. Starting with bauxite, show by equations how you could prepare aluminium sulfate.
6. What would be the effect of washing aluminium cooking vessels with strongly alkaline soap?
7. A solution of ammonium sulfide is added to a solution of aluminium sulfate. What is the composition of the precipitate?
8. How would you expect aluminium to act upon solutions of the following compounds: potassium hydroxide, calcium chloride, sulfuric acid, ferrous sulfate?

## PROBLEMS

1. The bauxite from a certain locality was found to contain 10 per cent iron oxide and 90 per cent  $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ . What weight of aluminium could be obtained from 1 ton of this ore?
2. What weight of aluminium sulfate can be obtained from 100 kg. of kaolinite?
3. What per cent of the crystalline potassium alum is water of crystallization?
4. (a) What weight of anhydrous ammonium alum is necessary to liberate the carbon dioxide from 100 g. of baking soda? (b) Calculate the volume of the carbon dioxide liberated, at  $100^\circ$  and 740 mm.
5. 100 kg. of aluminium nitride would yield what weight of ammonia?
6. What weight of aluminium carbide is necessary for the preparation of 10 l. of methane measured over water at  $20^\circ$  and 750 mm.?

## CHAPTER XXXVII

### THE SILICATE INDUSTRIES

**The ceramic industries.** There are a considerable number of industries which are based upon the use of clay, sand, limestone, and feldspar in varying degrees of purity, and in as far as they involve chemical transformations they are closely allied. To a greater or less extent they depend upon the formation of silicates from the materials named, the bases being chiefly oxides of sodium, potassium, calcium, magnesium, aluminium, and iron. These industries are often designated collectively as the *ceramic industries*. They may be roughly grouped into three classes, according to whether they are most intimately related to the manufacture of glass, cement, or clay products.

**Glass.** A glass is essentially a material which, on cooling from the state of a viscous liquid, has failed to crystallize and yet has become a rigid body. Pure quartz, when fused and cooled, is an example of the simplest of glasses. The ordinary commercial varieties of glass are mixtures of various silicates, together with excess of silica. When melted these all mix to form a homogeneous liquid, and when this is cooled, it gradually hardens to a glass.

1. *Ingredients of glass.* The ingredients employed in making ordinary glass such as window glass and bottles are sand, limestone, and the carbonate or sulfate of sodium. When a mixture of these materials in the proper proportion is heated to fusion, the volatile anhydrides are driven out by the silica (p. 494) and the bases remain in the form of silicates. For glasses of fine quality pure materials must be used, while for cheap bottle glass ordinary sand, limestone, and soda ash will serve. When sodium sulfate is used in place of sodium carbonate, carbon is added to reduce the sulfate to sulfite, which is more easily

decomposed by the silica. Arsenic trioxide is sometimes added. It forms bubbles on volatilization, and these appear to assist in collecting the smaller bubbles of other gases that are always present in the melt, which then escape and leave the glass clear.

2. *Varieties of glass.* By the proper selection and proportioning of the ingredients a great variety of glasses can be made. Ordinary window glass is essentially a sodium-calcium-magnesium glass, and as a rule its composition closely approximates the percentages required by the formula  $\text{Na}_2\text{O} \cdot \text{CaO} \cdot 6 \text{SiO}_2$ . Since it is made from ordinary limestone, which always contains magnesium, a variable percentage of magnesium oxide replaces a corresponding percentage of calcium oxide in the formula. For chemical glassware such as beakers and flasks it is necessary to use such materials as will give a product that resists the action

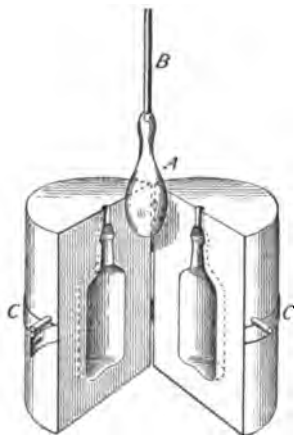


FIG. 165

of water and chemical reagents. In making such glass, from 5 to 10 per cent of boric oxide is generally used along with the silica, so that the product is essentially a borosilicate of different metals, with excess of silica. Thus the glass known as *non-sol* is a sodium-zinc-magnesium-aluminium borosilicate, while the *Fry* ware contains a small amount of calcium in addition. The *pyrex*, made to withstand shock and sudden changes of temperature, is a sodium-aluminium borosilicate containing an excess of silica. The *Jena* glass used so largely before the World

War is a zinc-sodium-aluminium borosilicate. The addition of lead oxide makes a soft glass, but one which is very brilliant and has a high refractive index suitable for some optical purposes.

**Molding and blowing of glass.** The way in which the melted mixture is handled in the glass factory depends upon the character of the article to be made. Many articles, such as bottles, are made by blowing the plastic

glass either by the mouth or by compressed air into hollow molds of the desired shape. The mold is first opened, as shown in Fig. 165. A lump of plastic glass *A* on the hollow rod *B* is lowered into the mold, which is then closed by the handles *C*. By blowing into the tube the glass is expanded into the shape of the mold. The mold is then opened and the bottle lifted out. The neck of the bottle must be cut off at the proper place and the sharp edges rounded off in the flame.

Other objects, such as lamp chimneys, are made by getting a lump of plastic glass on the end of a hollow iron rod and blowing it into the desired shape without the help of a mold, great skill being required in the manipulation of the glass.

Window glass is made by forming large hollow cylinders either by mouth or by machine. These cylinders are cut longitudinally and are then placed in an oven and heated until they

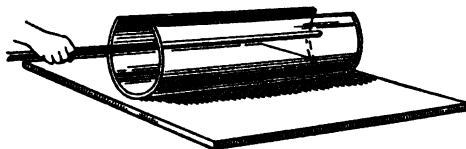


FIG. 166

soften, when they are flattened out into plates (Fig. 166). Plate glass is cast into flat slabs, which are then ground and polished to perfectly plane surfaces. Automatic machines are gradually replacing the older hand and mouth processes for making glassware of all kinds.

3. *Color of glass.* The color of glass is usually due to the presence of colored metallic silicates. For example, ferrous silicate colors the glass green, while ferric silicate colors it yellow or brown. The green color can be changed to the less objectionable yellowish tint by the addition of manganese dioxide, which acts as an oxidizing agent, converting the ferrous compounds into ferric. Cobalt compounds form deep-blue silicates, and many other metals impart characteristic colors. Sometimes the metals themselves are added and form a colloidal dispersion. Copper and gold are added to glass to produce a rich, ruby-red color. Selenium also gives a beautiful red color to glass and is used both to produce this color and to compensate for the green of ferrous silicate. Opaque, or milky, glasses are made by adding materials which remain suspended as solids in the melt, or which melt along with the glass but do not mix with it. In the latter case an emulsion is formed, and the turbid glass remains opaque on cooling. Fluorite, cryolite, bone ash, and tin oxide are used in this way.

**Optical glass.** Previous to the World War the United States imported from Germany practically all of the glass used in making the lenses required in microscopes, cameras, binoculars, and other optical instruments. When war was declared this supply was cut off, and it became urgent for the United States to develop the industry in order to secure an adequate supply of the glass for the construction of gun sights, periscopes, cameras, binoculars, — all of which instruments were of the greatest importance in the prosecution of the war. The composition of the different kinds of optical glass could easily be determined by analysis. The trouble lay in the difficulty of securing pure materials, not only for making the glass itself but also in the construction of the glass pots in which the operation is carried out; also in discovering the proper mechanical methods for carrying on the operation. For, if any iron is present in the materials, the resulting glass has some color, while if the operation is not carried on in the right way the glass is not homogeneous, and either of these defects is fatal for optical glass. It is sufficient to say that the problem was solved, and before the close of the war the United States had a supply of optical glass in excess of its needs.

**Cement.** The term *cement*, as ordinarily used at present, is applied to those mortars known more specifically as the hydraulic cements, which possess the property of hardening in water as well as in air. These cements are silicate bodies, usually very highly basic in character, which, when ground fine and mixed with water, undergo complex reactions resulting in the formation of a hard, rocklike mass. A number of different classes of cements are known, the most important of which is the so-called *Portland cement*.

**Composition of Portland cement.** The essential ingredients of Portland cement, together with the limits of each ingredient, are given by Bleining as follows:

INGREDIENTS	MINIMUM PER CENT	MAXIMUM PER CENT
SiO <sub>2</sub> . . . . .	19	26.0
Al <sub>2</sub> O <sub>3</sub> . . . . .	4	11.0
Fe <sub>2</sub> O <sub>3</sub> . . . . .	2	5.0
CaO . . . . .	58	67.0
MgO . . . . .	0	5.0
SO <sub>3</sub> . . . . .	0	2.5
Na <sub>2</sub> O + K <sub>2</sub> O . . . . .	0	3.0

**Manufacture of Portland cement.** The materials most commonly employed are limestone or marl and clay or shale. In general, however, any substance may be used which furnishes the ingredients listed in the above table. Among the substances so used is blast-furnace slag, which is an impure calcium aluminium silicate. The materials to be used are coarsely ground and then mixed together in the proper proportions and finely pulverized. The resulting mixture is run into a furnace and burned to a temperature just short of fusion, at which temperature it vitrifies, forming a grayish mass known as *clinker*. The process of silicate formation is not as complete as in the case of glass, but definite compounds are formed, among them being those represented by the formulas  $3 \text{CaO} \cdot \text{SiO}_2$ ,  $2 \text{CaO} \cdot \text{SiO}_2$ ,  $3 \text{CaO} \cdot \text{Al}_2\text{O}_3$ . Finally, the clinker is ground to a fine powder. Gypsum is often added in the process; this acts as a negative catalyzer, retarding the hardening, or setting, of the cement.

**The setting of cement.** The reactions which take place upon the addition of water to cement, and which result in the formation of a hard, rocklike mass, are not at all thoroughly understood. The complex substances apparently undergo hydrolysis when they come in contact with water. The resulting compounds unite with water to form crystalline hydrates, producing the hard, compact mass. Apparently some of the hydrated compounds form a jelly in which the interlacing crystals grow. The process of setting takes place best in air, but when wholly or partially completed, the mass may be placed under water, since the compounds present are all insoluble.

**Clay products.** The crudest forms of clay products, such as porous brick and draintile, have little chemistry involved in their manufacture. Naturally occurring clay is molded into the required form, dried, and then burned in a kiln, but not to a temperature at which the materials soften. In this process the nearly colorless ferrous compounds in the clay are converted into ferric compounds, which give the usual red color to these articles. In making vitrified brick the temperature is raised to

the point at which fusion begins, so that the brick is partially changed to a kind of glass.

**White pottery.** This term is applied to a variety of articles varying from the crudest porcelain to the finest chinaware. While the processes used in the manufacture of the articles differ in details, fundamentally they are the same and may be described under three heads: (1) the preparation of the body of the ware, (2) the process of glazing, and (3) the decoration.

1. *The body of the ware.* The materials used consist of an artificially compounded clay made from kaolin, plastic clay, pulverized quartz (known as Potter's flint), and pulverized feldspar. This mixture is plastic and is worked into the desired shape by molds or on a potter's wheel. The ware is then dried and burned until vitrified, and in this form is known as *bisque*. This is usually porous and hence must be glazed to render it nonabsorbent.

2. *The glaze.* The glaze is a fusible glass which is melted over the surface of the body. The constituents of the glaze are quartz, feldspar, clay, and various metallic oxides, often mixed with a little boric oxide. These materials are finely ground and mixed with water to a paste. Sometimes they are first fused into a glass, which is then powdered and made into the paste. The *bisque* is dipped into the glaze paste, dried, and fired until the glaze materials melt and flow evenly over the surface. The glaze must be so chosen as to resist the reagents to which it is to be exposed, and it must have the same coefficient of expansion as the body; otherwise it will check or crackle when the vessel is exposed to changes of temperature. The calculation of a glaze for a given body evidently requires a very thorough knowledge of the physical constants of the clay from which the body was made, as well as of the properties contributed to the glaze by each ingredient.

3. *The decoration.* If the article is to be decorated, the design may either be painted upon the body before glazing, when it is said to be underglazed, or it may be painted upon the glaze and the article fired again, the pigments melting into the glaze. In the latter case it is said to be overglazed. In the former case the pigments used are, as a rule, metallic oxides, while in the latter case they are often colored glasses.

4. *Ancient glazes and enamels.* It is a widespread belief that the ancients and Orientals were able to produce glazes, enamels, and glasses that in loveliness surpass the best efforts of modern times. This is an error. Modern knowledge and skill can reproduce and even exceed any effect achieved in the past. Patience in securing artistic designs is the only point of superiority of the Orientals.

## QUESTIONS

1. What are the advantages and the disadvantages of glass made from pure silica?
2. Why is window glass blown but plate glass molded?
3. What is the distinction between kaolinite, kaolin, and clay?
4. The glass in windows appears colorless. How can you easily prove that it has considerable color?
5. What is the distinction between mortar, plaster, and cement?
6. Why not use window glass in making chemical glassware such as beakers and flasks?
7. Why not use sodium silicate as a glass?
8. Why should a sulfite be more easily decomposed by silica than a sulfate?

## PROBLEMS

1. Calculate the percentage composition of kaolinite.
2. In what proportion must the raw materials be mixed so as to secure a glass of the composition expressed by the formula  $\text{Na}_2\text{O} \cdot \text{CaO} \cdot 6 \text{SiO}_2$ , assuming that the limestone used is 98 per cent calcium carbonate?

## CHAPTER XXXVIII

### THE IRON FAMILY

	SYMBOLS	ATOMIC WEIGHT	DENSITY	MELTING POINT	OXIDES
Iron . . . . .	Fe	55.84	7.86	1530°	FeO, Fe <sub>2</sub> O <sub>3</sub>
Cobalt . . . . .	Co	58.97	8.60	1480°	CoO, Co <sub>2</sub> O <sub>3</sub>
Nickel . . . . .	Ni	58.68	8.90	1452°	NiO, Ni <sub>2</sub> O <sub>3</sub>

**The family.** The elements iron, cobalt, and nickel bear a relation to one another which is different from that existing among the members of any other family as yet considered. Their atomic weights are very close together, and in the periodic table they are placed in one family, not because the plan of arrangement brings them together, but because they are so similar (p. 333) and evidently constitute a natural family.

Iron is noteworthy as the first metal to be described in detail which exerts two different valences and forms two series of salts. In the *ferrous salts* the iron is bivalent, and in many respects ferrous salts resemble those of magnesium; in the *ferric salts* the iron is trivalent, the ferric salts resembling those of aluminium. It is therefore appropriate to consider iron at the present time. It is also worthy of note that the metals which remain to be considered are isolated by reduction of their oxides or from their sulfides, and not by electrolytic methods.

### IRON

**Occurrence.** Iron has long been known, since its ores are very abundant and it is not difficult to prepare the metal from them in fairly pure form. It occurs in large deposits as oxides, sulfides, and carbonates, and in smaller quantities in a great variety

of minerals. Indeed, very few rocks and soils are free from small amounts of iron, and it is assimilated by both plants and animals. It is a constituent of both chlorophyll and hæmoglobin, and plays a fundamental part in life processes.

**Preparation of pure iron.** Pure iron may be prepared in the form of a fine powder by heating the oxide in a current of hydrogen, though the product contains adsorbed hydrogen unless the process is carried out at a higher temperature. It may be obtained in coherent masses by the electrolysis of ferrous sulfate between iron electrodes. To prevent the adsorption of hydrogen, which makes the metal hard and brittle, it is necessary to conduct the electrolysis at about  $100^{\circ}$  and to add some calcium chloride to the electrolyte. By such methods Burgess has obtained iron said to be 99.98 per cent pure.

**Properties of pure iron.** Pure iron is a silvery metal having a density of 7.86 and a melting point of  $1530^{\circ}$ . It is ductile and malleable and is almost as soft as aluminium. It is especially well adapted to the manufacture of electromagnets, since it acquires and loses magnetic properties much more rapidly than do the ordinary varieties of iron. It is not acted upon to any extent by air and hence is adapted for purposes where resistance to corrosion is desired.

**The iron of commerce.** Iron differs from most of the other metals used in the industries in that the pure metal is rarely obtained and is of limited application, while that which contains small percentages of other elements exhibits a wide variety of properties and is of the greatest importance. Carbon is always present in quantities which range from mere traces up to 7 per cent. According to the conditions under which the metal is produced, this carbon may be in the form of graphite scattered through the iron, or as a solid solution of carbon in iron, or in combination with the iron in the form of a carbide. The most important of these carbides has the formula  $\text{Fe}_3\text{C}$  and is a hard, brittle substance known as *cementite*. Manganese and silicon, together with traces of phosphorus and sulfur, are also present.

The properties of iron are much modified by the percentages of these constituents, by their form of combination in the iron, and by the treatment of the metal during its production from the ore. Accordingly many varieties of iron are recognized in commerce, the chief of which are *cast iron*, *wrought iron*, and *steel*.

**The metallurgy of iron.** The problem to be solved in the production of commercial iron is (1) to obtain a metallic alloy of the requisite chemical composition and physical properties and (2) to produce it on a very large scale. The development of the huge modern furnaces has demanded a wonderful application of chemical knowledge to a definite purpose and a no less wonderful engineering skill in securing the present great scale of production. To understand the processes to be described it will be necessary to remember constantly that large and rapid production is fully as necessary as great purity.

**Materials used in metallurgy of iron.** Four different classes of materials are used in the metallurgy of iron:

1. **Iron ore.** The ores most frequently employed are *hematite* ( $\text{Fe}_2\text{O}_3$ ); *siderite* ( $\text{FeCO}_3$ ); *limonite* ( $2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ ); *magnetite* ( $\text{Fe}_3\text{O}_4$ ). As mined for use all ores contain earthy matter and often sulfides and phosphates as well.

While iron ore is mined in a number of different localities in the United States, the great center of production is in the neighborhood of Lake Superior, the ore being chiefly *hematite*. Large amounts are also mined near Birmingham, Alabama.

2. **Carbon.** Carbon in some form is necessary both as a *fuel* and as a *reducing agent*. In former times wood charcoal was used to supply the carbon, but now coke is almost universally used.

3. **Hot air.** To maintain the high temperature that is required for the reduction of iron, a very active combustion of fuel is necessary. This is secured by forcing a strong blast of *hot air* into the lower part of the furnace during the reduction process.

4. **Flux.** All the materials which enter the furnace must leave it again, either in the form of gases or as liquids. The *iron* is drawn off as the liquid metal after its reduction, the *oxygen* with

which it was combined escaping as oxide of carbon. To secure the removal of the *earthy matter* charged into the furnace along with the ore, materials are added to the charge which will combine with the impurities in the ore, forming a liquid. The material added for this purpose is called the *flux*, and the liquid produced from the flux and the ore is called *slag*.

**The slag.** The slag is a variety of difficultly fusible glass, being essentially a calcium-aluminium silicate. If the ore is rich in silica, as is usual, limestone is used as a flux; if the ore contains limestone, silica or feldspar is used; if the ore is very pure, both constituents must be added as flux.

The formation of slag converts the oxides of calcium, magnesium, aluminium, and silicon contained in the ore into the liquid state, and not only does this make the removal of these materials easy, but the liquid is a necessity for other reasons. It is a medium in which the little droplets of iron run together into one large mass; it keeps the contents of the furnace fused and so prevents clogging; it floats over the collected iron and prevents its oxidation. In every operation in which iron is melted a slag must be provided.

**Cast iron.** Ordinarily the first step in the manufacture of any variety of commercial iron is the production of *cast iron*. The ores are mixed with a suitable flux and are reduced by heating with coke.

**Blast-furnace process.** The reduction is carried out in a large tower called a blast furnace (Fig. 167). This is usually 80 ft. high and 20 ft. in internal diameter at its widest part, narrowing somewhat toward both the top and the bottom. The walls are built of steel and are lined with fire brick. The base is provided with a number of pipes *A*, called *tuyères*, through which hot air is forced into the furnace. The tuyères are supplied from a large pipe *B*, which girdles the furnace. At the base of the furnace is an opening, through which the liquid metal can be drawn off from time to time. There is also a second opening *C*, somewhat above the first, through which the excess of slag overflows. The top is closed by a movable trap *D* called the *bell*, and through this the materials to be used are introduced. The gases resulting from the combustion of the fuel and the reduction of the ore, together with the nitrogen of the air admitted through

the tuyères, escape through pipes *E*. These gases have a temperature of about  $300^{\circ}$  and contain a sufficient percentage of carbon monoxide to render them combustible; they are accordingly utilized for heating the blast of air admitted through the tuyères and as fuel for the engines.

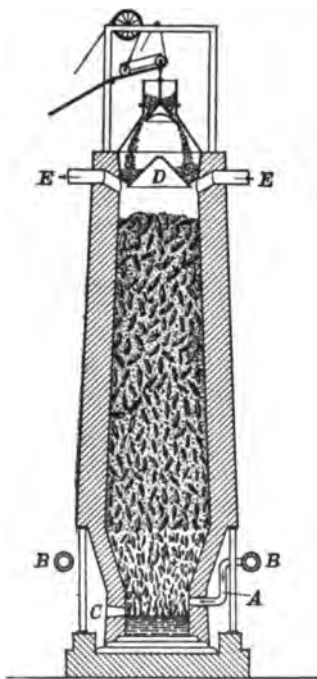


FIG. 167

Charges consisting of coke, ore, and flux in proper proportion are at intervals introduced into the furnace through the bell. At the bottom of the furnace the coke burns fiercely in the hot-air blast, forming carbon dioxide, which is at once reduced to carbon monoxide as it passes over the highly heated carbon.

The temperature of the furnace at the point at which the hot air enters is about  $1600^{\circ}$ , but gradually decreases toward the top of the furnace, at which it is only from  $300^{\circ}$  to  $400^{\circ}$ . Reduction of the ore begins at the top of the furnace through the action of the carbon monoxide. As the ore slowly descends the reduction is completed and the resulting iron melts and collects as a liquid in the bottom of the furnace, the lighter slag floating above it. After a considerable quantity of iron has collected, the slag is drawn off through *C*, and the iron is run out into ladles and taken to the converters for the manufacture of steel; or it is run into sand molds and cast into ingots

called *pigs*. The process is a continuous one, and when the furnace is once started, it is kept in operation for months without interruption. The iron is withdrawn at intervals of about six hours.

**Properties of cast iron.** The product of the blast furnace is called *cast iron*. It varies considerably in composition, but always contains over 2 per cent of carbon, variable amounts of silicon, and at least traces of phosphorus and sulfur. Two extreme varieties of cast iron are recognized, *gray* iron and *white* iron. In gray iron the carbon is present partly in the form of cementite and partly as graphite, the latter of which gives the metal its gray color. In white cast iron almost all the carbon is in the combined

state in the form of cementite; hence this variety is much harder and more brittle than the gray iron. Between these two extreme types there are all intermediate varieties. Cast iron is hard and brittle and melts at about  $1100^{\circ}$ . It cannot be welded or forged but is easily cast in sand molds. It is rigid but not elastic, and its tensile strength is small. It is used for making castings and in the manufacture of other varieties of iron. Cast iron, especially those grades of high silica content, is not acted upon by acids to the same extent as the purer grades of iron and so is used in making vessels for concentrating acids (p. 315) and for similar purposes.

**Wrought iron.** Wrought iron is made from cast iron by burning out most of the carbon, silicon, phosphorus, and sulfur which it contains.

The process is carried out in a puddling furnace. The floor of the furnace is covered with a layer of iron oxide, and on this is placed the charge of cast iron, together with some suitable flux (usually limestone). The fuel is burned in a fire box at the side of the furnace, and the flame is led over the charge of cast iron, the heat being reflected down upon it by a low, arching roof. The iron is soon melted, and the phosphorus and silicon are oxidized by the iron oxide, forming acid anhydrides, which combine with the flux or with the iron oxide to form a slag. The carbon and sulfur are also oxidized and escape as carbon dioxide and sulfur dioxide. As the iron is freed from other elements it becomes pasty, owing to the higher melting point of the purer iron, and in this condition forms small lumps, which are raked together into a larger one. The large lump is then removed from the furnace and rolled or hammered into bars, most of the slag being squeezed out in this process.

**Properties of wrought iron.** Wrought iron has a fibrous structure, being composed of fibers of pure iron (*ferrite*) separated by a small percentage of slag. The ferrite present contains less than 0.3 per cent of carbon and small amounts of other elements. Wrought iron is soft, malleable, and ductile. While its tensile strength is greater than that of cast iron, it is less than that of most steel. Its melting point is much higher than that of cast iron. Wrought iron is no longer produced to the same relative extent as in former years, since soft steel can be made at less cost and has almost the same properties.

**Steel.** Steel, like wrought iron, is made from cast iron by burning out a part of the carbon, silicon, phosphorus, and sulfur which it contains, but the processes used are different from that employed in the manufacture of wrought iron. Nearly all the steel of commerce is made by one of two general methods, known as the *Bessemer process* and the *open-hearth process*. There are two modifications of each of these processes, based upon the differences in the material used in the lining of the furnaces: (1) In the one the furnaces are lined with silica, which is an acid anhydride. This modification is therefore known as the acid process. In the steel made in these furnaces the carbon, manganese, and silicon are removed, but nearly all of the phosphorus and sulfur in the original cast iron are retained, since no fluxing material adapted to their removal is present. The acid process is employed when the cast iron to be used is very low in phosphorus and sulfur. (2) In the other modification the furnace is lined with limestone or dolomite, and this modification is known as the basic process. In such furnaces both the phosphorus and the sulfur are removed, together with the carbon and silicon. These furnaces are therefore employed when the cast iron contains appreciable percentages of phosphorus and sulfur. Practically all of the steel produced in the United States is made by either the acid Bessemer or the basic open-hearth process. A brief description of these methods follows.

**Acid Bessemer process.** This process, invented about 1860, is carried out in great egg-shaped crucibles called converters (Fig. 168), each one of which will hold as much as 15 tons of steel. The converter is built of steel and lined with silica. It is mounted on trunnions, so that it can be tipped over on its side for filling and emptying. One of the trunnions is hollow, and a pipe connects it with an air chamber *A*, which forms a false bottom to the converter. The true bottom is perforated, so that air can be forced in by an air blast admitted through the trunnion and the air chamber.

White-hot liquid cast iron from a blast furnace is run into the converter through its open, necklike top *B*, the converter being tipped over to receive it; the air blast is then turned on and the converter turned to a nearly vertical position. The carbon, silicon, and manganese in the iron are

rapidly oxidized (the silicon and manganese first and then the carbon), the oxidation being attended by a brilliant flame. The heat of the reaction, largely due to the combustion of silicon, keeps the iron in a molten condition. The air blast is continued until the character of the flame shows that all the carbon has been burned away. The process requires from 7 to 20 minutes, and when it is complete, the desired quantity of carbon (generally in the form of high-carbon iron alloys) and manganese or other deoxidizing elements are added and allowed to mix thoroughly with the fluid. If it is desired to obtain a product rich in silica or other alloying materials, these are also added at this point in the form of iron alloys such as ferrosilicon (p. 489). The converter is then tilted (Fig. 169), and the steel run into molds, and the ingots so formed are hammered or rolled into rails or other objects.

**Basic open-hearth process.** Fig. 170 shows the simpler parts of the type of furnace used in this process. The hearth of the furnace is about 40 ft. in length, 12 ft. in width, and 2 ft. in depth, and is lined with limestone or dolomite *A, A*. Either gas or sprayed oil is used as fuel. Below the furnace is placed a checkerwork of brick so arranged that the hot products

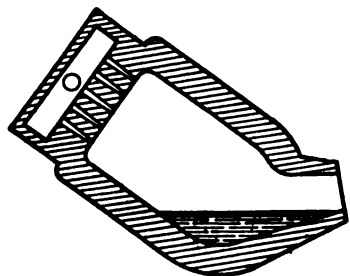


FIG. 169

vigorous combustion ensues, the flame passing above and over the cast iron, steel scrap, and lime with which the furnace is charged. The products of combustion escape through *E* and *F*. At the temperature reached the

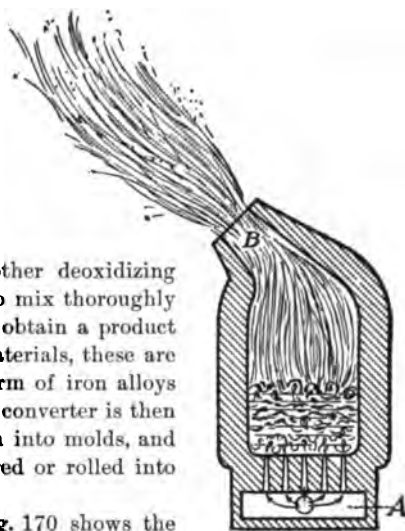


FIG. 168

of combustion escaping from the furnace may be conducted through it, thus heating the bricks to a high temperature. Both the air necessary for combustion and the gaseous fuel (unless decomposed by heating, as in the case of natural gas and sprayed oil) are preheated by passing them over the hot bricks, so that the temperature reached during combustion is greatly increased. The gas entering through *C* comes in contact at *D* with the hot air entering through *B*, and a

carbon in the cast iron is removed in the form of the oxide, the escaping gas giving the melted metal the appearance of boiling. The silicon, phosphorus, and sulfur unite with oxygen to form acid anhydrides; these combine with the lime to form a slag, and this rises to the surface of the melted charge and is easily removed. When a test shows the desired

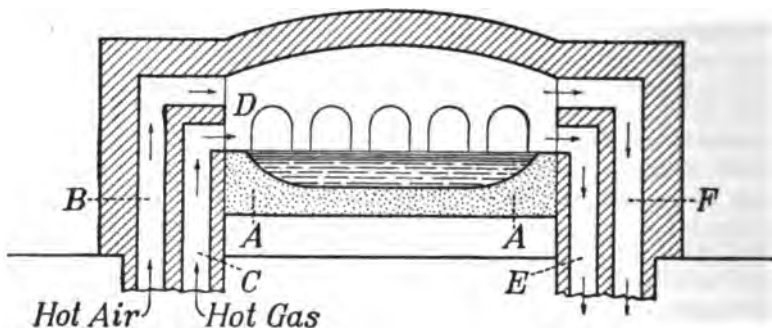


FIG. 170

percentage of carbon present, the melted steel is run into large ladles, along with the requisite deoxidizing and alloying elements, and then into molds. An average furnace produces about 50 tons of steel in a given charge, approximately 8 hours being required in the process. At present by far the largest amount of steel produced in the United States is made by this process.

**Properties of steel.** Steel contains from a trace up to 2 per cent of carbon, less than 0.2 per cent of silicon (except in special cases), and not more than traces of phosphorus and sulfur. When desired, steel may be made so pure that it contains only traces of carbon. Indeed, a product containing 99.85 per cent of iron is now being made by the open-hearth process. Such steel is very soft. As the carbon content rises the steel becomes harder and less ductile; at the same time the tensile strength increases until the carbon amounts to about 1.1 per cent, after which it decreases. Steel can be rolled into sheets, cast in molds and forged into desired shapes.

**Tool steel, or crucible steel.** Steel designed for use in the manufacture of edged tools and similar articles should be relatively free from silicon and phosphorus, but should contain

from 0.5 to 1.5 per cent of carbon. The percentage of carbon should be regulated by the exact use to which the steel is to be put. Steel of this character is usually made in small lots from either Bessemer or open-hearth steel in the following way.

A charge of melted steel is placed in a large crucible and the calculated quantity of pure carbon is added. The carbon dissolves in the steel, and when the solution is complete the metal is poured out of the crucible. This is sometimes called *crucible steel*.

**Electrothermal metallurgy of steel.** An increasing quantity of high-grade tool steel is being produced in electrical furnaces. The furnace is heated by electrical energy, and a large quantity of steel can be kept melted in these furnaces as long as may be desired. The electrical current is used merely to produce heat, so that the process is not dependent upon electrolysis. This method is almost identical with the open-hearth method, save in the way in which the heat is supplied, and produces the same kind of steel as does the latter method.

**Relation of the three varieties of iron.** Wrought iron consists of fibers of nearly pure iron (ferrite) separated by traces of slag, while most steel contains an appreciable amount of alloy material (chiefly carbon) and cast iron contains still more of the same substances. It is impossible, however, to assign a given sample of iron to one of these three classes on the basis of its chemical composition alone. For example, a low-carbon steel may contain less carbon than a given sample of wrought iron. *The classification of commercial iron into cast iron, wrought iron, and steel is really based on the method of manufacture. The product of the blast furnace is cast iron, that of the puddling furnace is wrought iron, that of the Bessemer and open-hearth processes is steel.*

**The hardening and tempering of steel.** When steel containing from 0.5 to 1.5 per cent of carbon is heated to a relatively high temperature and then cooled suddenly by plunging it into cold water or oil, it becomes very hard and brittle. When gradually reheated and then slowly cooled, this hardened steel becomes softer and less brittle, and this process is known as *tempering*.

By properly regulating the temperature to which the steel is reheated in tempering, it is possible to obtain almost any condition of hardness demanded for a given purpose, as for making springs or cutting tools. Steel assumes different color tints at different temperatures, and by these the experienced workman can tell when the desired temperature has been reached. Lake gives the following temperatures as suited to the tempering of the tools specified:

220°—paper cutters, wood-engraving tools	275°—axes, springs
240°—knife blades, rock drills	290°—needles, screw drivers
260°—hand-plane cutters and cooper's tools	300°—wood saws.

**Steel purifiers.** The great difficulty in securing a good steel is (1) to accomplish the complete reduction of the oxide and (2) to prevent the absorption of gases which cause blowholes as the casting solidifies. These difficulties are avoided, as far as possible, by adding to the steel, at the close of the operation, certain elements which will combine with the oxygen and the absorbed gases. The compounds formed pass into the slag, and almost none of the added element remains in the finished product. Aluminum is used to a large extent for this purpose, as are also vanadium and titanium in the form of iron alloys. Such elements are called *deoxidizers*, *purifiers*, or *scavengers*.

**Steel alloys.** It has been found that small quantities of a number of different elements, when added to steel, very much improve its quality for certain purposes. Among the elements most used in this way are manganese, silicon, nickel, chromium, tungsten, molybdenum, vanadium, titanium, cobalt, and uranium. These elements may act in two different ways. Some of them, such as titanium and vanadium, act mainly as purifiers, their function being to remove any gases (chiefly oxygen and nitrogen) dissolved in the iron. Others, such as nickel and chromium, form alloys with the steel, the properties of which vary according to the element present. Thus nickel renders the steel harder and increases its tensile strength and elastic limit, while chromium and tungsten, molybdenum and cobalt cause the steel to keep its temper at high temperatures, so that such alloys are adopted for use in the construction of high-speed lathe tools. Silicon forms an alloy with iron which is only slightly attacked by acids, and this property makes the alloy useful for many purposes.

The approximate composition and the uses of some of these steel alloys are as follows:

8.5% nickel . . . . .	armor plate
3.5% nickel and 3.5% chromium . . . . .	armor plate and projectiles
12.0% manganese . . . . .	burglar-proof safes
5.0% chromium and from 8 to 24% tungsten or 10% molybdenum or cobalt . . . . .	high-speed lathe tools
0.1% titanium . . . . .	car rails and steel castings
0.1% vanadium . . . . .	automobile parts
70.0% cerium . . . . .	gas and cigar lighters
0.2% vanadium, 3.5% nickel, 0.75% chromium, and 0.4% manganese . . . . .	automobile springs and axles
12 to 15% silicon (duriron and tantiron) . . . . .	retorts for distilling acids

**Passive iron.** Iron readily dissolves in both dilute and concentrated nitric acid, but when it is brought into contact with fuming nitric acid, that is, with nitric acid containing nitrogen dioxide in solution, it loses many of its characteristic properties and is then said to be in a *passive state*. For example, such iron is no longer attacked by dilute nitric acid, nor does it precipitate copper and silver from solutions of their salts, as does ordinary iron. The metal loses its passivity when it is rubbed, scratched, or given a sharp blow, or when certain other metals are brought into contact with it. A number of other metals, including cobalt, nickel, and chromium, act in a similar way. No entirely satisfactory explanation has been offered to account for this phenomenon. According to one assumption the nitric acid forms a thin protective film of metallic oxide over the metal. This view receives

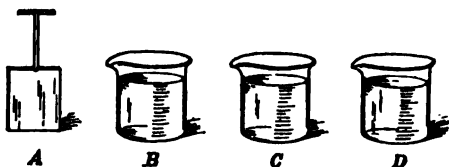


FIG. 171

support from the fact that other oxidizing agents may be substituted for nitric acid in rendering iron passive. The passivity of iron may be illustrated in the following simple way: A piece of sheet iron *A* (Fig. 171) is immersed for a few moments in fuming nitric acid contained in *B*. It is next lowered into pure water in *C*, in order to wash off the adhering acid. Finally, it is dipped for a moment into a solution of copper sulfate in *D*. Apparently no change takes place. If now the iron is struck a sharp blow, it at once loses its passivity and regains its normal property of replacing copper from copper sulfate, as is evidenced by the rapid formation of a thin film of the metal over the entire surface of the iron.

**The rusting of iron.** A number of different theories have been advanced to account for the changes taking place in the rusting of iron. The most satisfactory of these is known as the electrolytic theory. According to this the primary reaction in the rusting of iron is between iron and water, as expressed in the following equation:

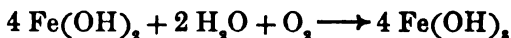


The ions  $\text{Fe}^{++}$  and  $2 \text{OH}^-$  then combine to form ferrous hydroxide ( $\text{Fe}(\text{OH})_2$ ). This is further acted upon by oxygen and moisture, and forms the complex substance known as iron rust. It is evident that the composition of rust will vary according to the conditions of its formation.

**Compounds of iron.** The compounds of iron are much more numerous than those of any metal so far considered, for not only does iron form two series of simple salts, but it is a constituent of many complex salts as well. It will be possible to mention only a few typical individuals in each class.

**Ferrous compounds.** The ferrous salts, resembling those of magnesium not only in formula but often in degree of hydration, are usually nearly white when prepared by precipitation, but are colored some shade of light green or yellow when well crystallized. They are not very greatly hydrolyzed in solution, since ferrous hydroxide is about as strong a base as the hydroxide of magnesium or of zinc, but they are readily oxidized, as will be explained later. The soluble salts are most easily prepared by dissolving iron in the appropriate acid, and the insoluble salts by precipitation.

**Ferrous hydroxide ( $\text{Fe}(\text{OH})_2$ ); ferrous oxide ( $\text{FeO}$ ).** Ferrous hydroxide ( $\text{Fe}(\text{OH})_2$ ) forms as a white, nearly insoluble precipitate when a solution of a ferrous salt is treated with a soluble base. On exposure to the air and moisture it quickly oxidizes to ferric hydroxide:

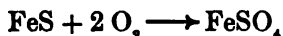


When heated out of contact with air, it is converted into ferrous oxide ( $\text{FeO}$ ). The latter compound is more easily obtained as a black, combustible powder by heating ferrous oxalate:



**Ferrous chloride ( $\text{FeCl}_2$ ).** Anhydrous ferrous chloride is prepared by strongly heating iron in a current of hydrogen chloride, the salt condensing in the colder portions of the tube in white, pearly scales. It dissolves in water, with evolution of much heat, and from this solution crystallizes as the green tetrahydrate  $\text{FeCl}_2 \cdot 4 \text{H}_2\text{O}$ . The latter salt is more easily obtained by dissolving iron in hydrochloric acid and evaporating the solution out of contact with the air.

**Ferrous sulfate ( $\text{FeSO}_4$ ).** The sulfate is the most familiar ferrous salt and has important uses. It is easily prepared by dissolving iron in dilute sulfuric acid and evaporating to crystallization. It is then obtained in large monoclinic crystals of the composition  $\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$ , known as *green vitriol*, or *copperas*. In the industries it is obtained from the liquors which result from cleaning sheet steel with sulfuric acid preparatory to tinning or galvanizing the steel. It is also manufactured by the oxidation of the abundant mineral pyrite ( $\text{FeS}_2$ ), usually after a careful partial roasting, which converts the pyrite into ferrous sulfide ( $\text{FeS}$ ):



It is used as a disinfectant, as a reagent for killing weeds, in the dyeing industry, as a substitute for aluminium sulfate in water purification (p. 593), and in the manufacture of black inks.

**Inks.** Most of the common black inks are made by treating an extract of *nutgalls* with ferrous sulfate and adding a blue-black dye. The nutgalls are rich in *gallotannic acid*, and this, with ferric compounds formed by the oxidation of the ferrous sulfate by the air, gives a nearly black precipitate. The black dye gives a temporary color, the permanent color being developed after the writing has been exposed to the air. The addition of some colloidal material, such as gum arabic, together with a little sulfuric acid, prevents the precipitation of the black colloidal substance in the ink bottle. A preservative is usually added to prevent the ink from molding.

**The vitriols.** The term *vitriol* is applied to the hydrated sulfates of a number of bivalent metals. These compounds are of two distinct types: the one group forms monoclinic crystals which contain seven molecules of water of crystallization; the

other forms triclinic crystals with five molecules of water. All the salts in a given series are isomorphous, and many of the vitriols are dimorphous, crystallizing in both forms. The sulfates of iron, zinc, and magnesium are the most familiar representatives of the monoclinic vitriols, while copper sulfate ( $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ ) is the best-known triclinic vitriol.

**Ferrous ammonium sulfate** ( $(\text{NH}_4)_2\text{SO}_4 \cdot \text{FeSO}_4 \cdot 6 \text{H}_2\text{O}$ ). When ammonium sulfate and ferrous sulfate are brought together in solution in molecular proportions, a double salt of the formula  $(\text{NH}_4)_2\text{SO}_4 \cdot \text{FeSO}_4 \cdot 6 \text{H}_2\text{O}$ , known as *Mohr's salt*, separates on crystallization. This salt oxidizes less readily in the air than most other ferrous salts and is frequently employed in chemical analysis. All the sulfates which form vitriols yield similar double salts, not only with ammonium sulfate but also with the sulfates of potassium, rubidium, and caesium. The type of double salt represented by the general formula  $\text{M}'_2\text{SO}_4 \cdot \text{M}''\text{SO}_4 \cdot 6 \text{H}_2\text{O}$  therefore includes many individuals, all of which are isomorphous.

**Ferrous sulfide (FeS).** Ferrous sulfide is found in nature as the yellowish-brown mineral *pyrrhotite*, which nearly always contains an excess of sulfur in solid solution, amounting sometimes to as much as 6.5 per cent of the weight of the mineral. It is easily prepared by heating iron with sulfur or by treating a solution of a ferrous salt with a soluble sulfide:



Prepared in the latter way it is a black solid, insoluble in water but readily soluble even in very weak acids. It melts at about  $1175^\circ$  and is obtained as a liquid flux in some metallurgical processes (p. 478). It is used in the laboratory in the preparation of hydrogen sulfide.

**Iron disulfide (FeS<sub>2</sub>).** This compound occurs very abundantly in nature, especially in Spain. It is also found in the coal measures, often forming fossils of plants. The usual form is known as *pyrite*, *pyrites*, or *fool's gold*, and is a brass-yellow mineral, well crystallized in the isometric system. It is stable

at moderately high temperatures, whereas *marcasite*, a more silvery mineral of the same composition, is not stable above  $450^{\circ}$ . Little is known as to the structure of these compounds or the valence of the constituent elements. Pyrite is mined in very large quantities and is used as a source of sulfur dioxide in the sulfuric acid industry (p. 313).

**Ferrous carbonate ( $\text{FeCO}_3$ ).** As *siderite*, isomorphous with calcite, ferrous carbonate occurs rather abundantly in nature, often in large crystals. Prepared by precipitation it is a nearly white, crystalline powder. Like calcite, it is soluble in water containing carbon dioxide, and solutions of this kind constitute the *chalybeate mineral waters*.

**Ferric compounds.** In the ferric compounds iron acts as a trivalent metal; consequently, the formulas of these compounds resemble those of the corresponding compounds of aluminium. Ferric hydroxide ( $\text{Fe}(\text{OH})_3$ ) is a very weak base, and all the simple ferric salts are largely hydrolyzed, their solutions acquiring the reddish-brown color of the hydroxide. As a rule, the salts are not so well crystallized as those of the ferrous series, and they present a greater variety of color.

**Ferric hydroxide ( $\text{Fe}(\text{OH})_3$ ).** When a solution of a base is added to a solution of a ferric salt, a reddish-brown precipitate is obtained, which for convenience is given the formula  $\text{Fe}(\text{OH})_3$ . Like the corresponding compound of aluminium (p. 590) it is a colloidal gel and its composition varies with the exact conditions of its preparation. It is best to regard it as an oxide with varying degree of hydration. Iron rust is probably a mixture of such hydrated oxides. Ferric hydroxide is not appreciably dissolved by soluble bases.

**Ferric oxide ( $\text{Fe}_2\text{O}_3$ ).** When the hydroxide is strongly heated, it forms the oxide  $\text{Fe}_2\text{O}_3$ , which is an insoluble, earthy material occurring in nature in various forms of hematite, which range in color from red to black. The same compound is obtained in burning pyrite and, when carefully prepared, constitutes the pigment known as *Venetian red*, which, owing to its permanency, is much used for painting structures that are exposed to the

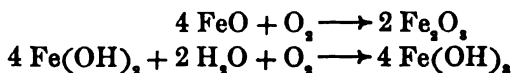
weather, such as bridges and railway cars. This oxide is also found in nature in combination with ferrous oxide, as the mineral *magnetite* ( $\text{Fe}_3\text{O}_4$ ), which appears to have the structure of a spinel (p. 591). It is sometimes called *magnetic oxide of iron*, or *loadstone*.

**Ferric chloride ( $\text{FeCl}_3$ ).** Ferric chloride is obtained in anhydrous form as a sublimate by heating iron in a current of chlorine. It is readily formed in solution by the usual methods, and crystallizes in a number of hydrated forms, the usual one having the formula  $\text{FeCl}_3 \cdot 6 \text{H}_2\text{O}$ . It is very soluble in water and to a less extent in other solvents, such as alcohol and ether. Its solution in alcohol constitutes the ordinary *tincture of iron* of the druggist.

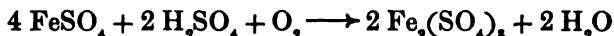
**Other soluble ferric salts.** Of the other soluble ferric salts a few deserve special mention. The *sulfate* ( $\text{Fe}_2(\text{SO}_4)_3$ ) can be obtained by the oxidation of green vitriol, as a white, poorly crystallized substance. With the alkaline sulfates it forms a series of violet-colored alums, which, owing to their well-crystallized condition, are the ferric salts most frequently used. The most familiar one is the *ferric ammonium alum* ( $\text{NH}_4\text{Fe}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$ ). The *nitrate* is deposited from concentrated solutions in well-formed, deliquescent crystals of the formula  $\text{Fe}(\text{NO}_3)_3 \cdot 9 \text{H}_2\text{O}$ , which have the same violet color as the alums. It is moderately soluble in dilute nitric acid, but readily forms supersaturated solutions. The *sulfocyanate* ( $\text{Fe}(\text{CNS})_3$ ) is a blood-red soluble salt, and its formation upon adding a sulfocyanate to a solution of unknown composition is a delicate test for the presence of ferric ions.

**Insoluble ferric compounds.** Most of the insoluble ferric compounds are basic salts of various kinds. The normal phosphate  $\text{FePO}_4$  is an exception to this and is found in nature in a number of forms. Neither the sulfide nor the carbonate is obtained by precipitation, since each is completely hydrolyzed, as in the case of the corresponding compounds of aluminium.

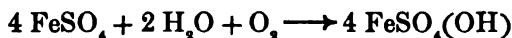
**Oxidation of ferrous salts.** When exposed to the action of oxidizing agents, especially in the presence of water, ferrous compounds are readily oxidized to the corresponding ferric compounds. This is illustrated in the case of the oxide and hydroxide:



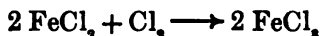
In a similar way, in the presence of sulfuric acid, ferrous sulfate is oxidized by an oxidizing agent, such as nitric acid:



In moist air the oxidation produces a basic ferric sulfate, thus:

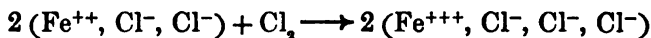


**Oxidation an increase in valence.** It will be noticed that in these reactions oxygen is used and the valence of the iron is increased from 2 to 3. *Any reaction which increases the valence of the metal of a compound is called an oxidation, even though no oxygen is involved in the process.* Thus, ferrous chloride is said to be oxidized to ferric chloride in the reaction expressed in the following equation:



Chlorine is said to be an oxidizing agent, since it effects the oxidation.

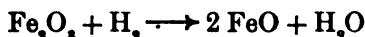
**Ionic oxidation.** If this same oxidation is represented as an ionic reaction, a still different view of oxidation is reached. In this case the equation may be written as follows:



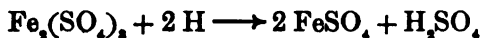
It will be seen that the charge upon the iron ion (cation) has increased from 2 to 3, while a corresponding number of chlorine ions (anions) have been formed from molecular chlorine. We shall meet with other reactions in which the charge upon the anion has been decreased while that upon the metal remains fixed. In both of the above cases the compound is said to be oxidized. From this point of view *oxidation may be defined as a reaction in which the charge upon the cation has been increased, or that upon the anion has been decreased.*

**Reduction of ferric compounds.** As the reverse of the oxidation reactions just described, all ferric compounds may, under

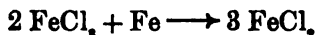
the proper conditions, be reduced to ferrous compounds. This is illustrated in the case of the oxide:



In solution many ferric salts are reduced by nascent hydrogen:

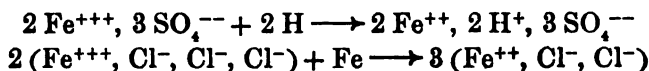


**Reduction a decrease in valence.** In these reactions the valence of the iron is diminished from 3 to 2, and the ferric compounds are said to be reduced even when neither oxygen nor hydrogen is concerned in the reaction. Thus the valence of the iron may be diminished by the action of a metal upon a ferric compound:



In general, then, a compound is said to be reduced when the valence of the metal present is diminished.

**Ionic reduction.** Representing the changes in the last two equations as ionic reactions, we have the equations:



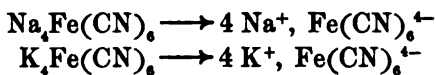
From this mode of representation it will be seen that the essential change in the reaction is the decrease in the charge of the iron cation from 3 to 2, and the reduction of an electrolyte may be defined as a reaction in which the charge of the cation is diminished, or that of the anion is increased.

**Complex compounds of iron.** Iron forms a large number of complex compounds, of which only the cyanides will be described. Iron forms no simple cyanides, but a very large number of complex cyanides are known, of which the ferrocyanide and ferricyanide of sodium and of potassium are the most important.

**Sodium ferrocyanide** ( $\text{Na}_4\text{Fe}(\text{CN})_6$ ); **potassium ferrocyanide** ( $\text{K}_4\text{Fe}(\text{CN})_6$ ). These two compounds are salts of the unstable ferrocyanic acid ( $\text{H}_4\text{Fe}(\text{CN})_6$ ). They are prepared from by-products obtained in the manufacture of coke. When the coal

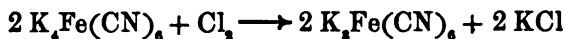
is heated in the absence of air, small amounts of the carbon, nitrogen, and hydrogen present are evolved in the form of hydrogen cyanide. This is absorbed and converted into calcium ferrocyanide by means of calcium hydroxide and the spent iron oxide employed in the purification of the gas evolved in the coking of the coal. The calcium ferrocyanide so obtained is converted into sodium or potassium ferrocyanide by treatment with appropriate salts of sodium or potassium. The reactions involved in the complete process are quite complex.

Both sodium ferrocyanide and potassium ferrocyanide are yellow in color and are readily soluble in water. The latter compound is often called *yellow prussiate of potash*. The sodium salt crystallizes from water in the form of the hydrate  $\text{Na}_4\text{Fe}(\text{CN})_6 \cdot 10 \text{H}_2\text{O}$ , while the potassium salt crystallizes as the hydrate  $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3 \text{H}_2\text{O}$ . In solution they ionize as follows:



It is important to notice that no ions of iron are present, so that these salts do not give the ordinary reactions for iron.

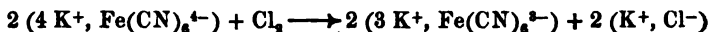
**Potassium ferricyanide ( $\text{K}_3\text{Fe}(\text{CN})_6$ ).** When potassium ferrocyanide in solution is treated with an oxidizing agent, a greenish solution is obtained, from which crystallize garnet-red crystals of the composition  $\text{K}_3\text{Fe}(\text{CN})_6$ , known as *red prussiate of potash*, or *potassium ferricyanide*. With chlorine as the oxidizing agent the equation is as follows:



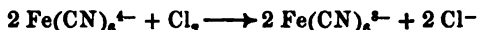
This compound in solution gives the ions  $3 \text{K}^+$  and  $\text{Fe}(\text{CN})_6^{3-}$  but no iron ions. Potassium ferricyanide is a salt of the unstable ferricyanic acid ( $\text{H}_3\text{Fe}(\text{CN})_6$ ).

**Oxidation and reduction of the iron cyanides.** The conversion of the ferrocyanide into the ferricyanide, and vice versa, is a very good illustration of oxidation and reduction in which the charge on the *cation* remains the same while that on the *anion* is altered.

1. *Oxidation of potassium ferrocyanide.* Written in ionic form the conversion of the ferrocyanide into the ferricyanide is expressed in the equation

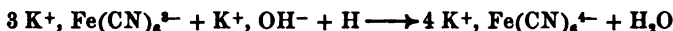


The number of  $\text{K}^+$  ions remains unchanged, and the essential features of the reaction are expressed in the simpler equation

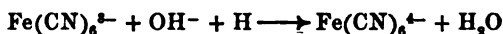


The charge on the anion is diminished from 4 to 3, a new ion ( $\text{Cl}^-$ ) being formed at the same time. In this case the anion acts as a *reducing agent* and is *itself oxidized*.

2. *Reduction of potassium ferricyanide.* In just the reverse way the ferricyanide may be reduced to the ferrocyanide:



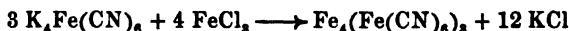
In this reaction, as in the former one, the number of the  $\text{K}^+$  ions in the solution remains unchanged, the essential feature of the reaction being the transfer of a negative electron from the hydroxyl ion  $\text{OH}^-$  to the ferricyanide ion  $\text{Fe}(\text{CN})_6^{3-}$ :



while at the same time an existing negative ion  $\text{OH}^-$  ceases to exist as an ion. In this case the anion  $\text{Fe}(\text{CN})_6^{3-}$  acts as an *oxidizing agent* and is *reduced*.

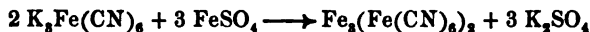
**Other complex cyanides.** Since the potassium in both ferrocyanide and ferricyanide acts as an ion, it is replaceable by other metals through double decomposition. Most of the ferrocyanides and ferricyanides so obtained are colloidal bodies insoluble in water and dilute acids. Copper ferrocyanide has already been mentioned in connection with its use as an osmotic membrane (p.188). The compounds obtained by treating these two salts with simple ferrous and ferric salts are of especial interest.

With potassium ferrocyanide and ferric chloride the equation is



The complex product of this reaction is an indigo-blue precipitate, known as *ferric ferrocyanide*, or *Prussian blue*. It is used largely as a pigment.

With potassium ferricyanide and ferrous sulfate the equation is



The resulting complex is of much the same color as Prussian blue and is known as *ferrous ferricyanide*, or *Turnbull's blue*. The formation of these two precipitates affords a delicate method not only for detecting the presence of iron in the form of its salts but also for distinguishing between ferrous and ferric salts.

**Blue printing.** When a ferric salt and potassium ferricyanide are brought together in solution, no precipitate forms, though the solution acquires a yellowish color. On exposure to the sunlight the ferric salt undergoes a partial reduction to ferrous salt, and a blue precipitate forms. Advantage is taken of these facts in the process of blue printing. A sensitive paper is prepared by soaking paper in a solution of potassium ferricyanide and a ferric salt (ferric ammonium citrate is generally used) and drying it in a dark place. When a black drawing on tracing cloth is placed upon such a sensitive paper and the two are exposed to the sunlight, the sensitive paper (except where it is protected by the black lines) turns a brownish color. It is then thoroughly washed with water to remove the soluble salts, the portions acted upon by the light turning blue, while the unaffected portions are left white. Both Prussian blue and Turnbull's blue are decomposed and thus decolorized by soluble bases, so that a solution of sodium bicarbonate can be used as an ink for white lettering on a blue print.

## COBALT

**Occurrence.** Most minerals containing cobalt are strongly suggestive of the presence of a heavy metal, yet the older metallurgists were unable to smelt them and obtain this metal. For this reason they named the metal *kobold*, meaning "goblin," and this gave us our name *cobalt*. The metal was finally obtained by the Swedish chemist Brandt in 1735. Cobalt usually occurs in combination with arsenic and sulfur, in complex minerals which also contain silver, iron, nickel, and copper. The simplest of these is *cobaltite* ( $\text{CoAsS}$ ). Such minerals are found sparingly in many localities, but the richest deposits are those located at Cobalt, Ontario. These are very rich in silver, and cobalt is worked up as a by-product, together with nickel and arsenic trioxide.

**Metallurgy and properties.** The metallurgy of the metal is very complicated, since it is difficult to separate cobalt and nickel. The pure metal is best prepared by the Goldschmidt process. It is a malleable, magnetic, silvery metal, which soon takes on a reddish tint upon exposure to the air. It melts at  $1480^{\circ}$  and has a density of 8.6. The metal is used chiefly in the form of alloys. *Cobalt steels* are used extensively in the construction of

high-speed cutting tools, since they retain their temper at high temperatures. *Stellite* is an alloy of variable composition, but the main constituents are cobalt, chromium, and tungsten.

**Oxides of cobalt.** Cobalt comes into the market very largely in the form of the black cobaltous oxide  $\text{CoO}$ , and in addition to this it forms two other oxides,  $\text{Co}_2\text{O}_3$  and  $\text{Co}_3\text{O}_4$ , corresponding to those of iron. Cobaltous oxide is a black powder used in making other cobalt compounds, blue glass, and blue decorations on china. When used as an ingredient in glasses, glazes, and enamels, it forms a blue silicate which has intense coloring properties. Sometimes the powdered blue glass called *smalt* is used instead of the oxide, and also for a pigment.

**Salts of cobalt.** Cobaltous oxide gives rise to a series of salts similar in formulas to the ferrous salts. In anhydrous form they are blue, but when hydrated they are usually cherry-red. The simple salts derived from cobaltic oxide, corresponding to the ferric salts, are very unstable, and few are well known. There are, however, a great many complex cobaltic salts. The hydrated *cobaltous nitrate*  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and *cobaltous chloride*  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  are the salts most frequently employed in the laboratory; both these salts are cherry-red in color. The *sulfide*  $\text{CoS}$  is formed as a black precipitate when a cobalt salt is treated with ammonium sulfide. It dissolves slowly in dilute acids, but much more rapidly in concentrated ones.

When potassium nitrite and a salt of cobalt are brought into solution and treated with dilute acetic acid, a complicated reaction takes place in which the cobalt is oxidized to the tervalent state by the nitrous acid liberated in the reaction and an insoluble yellow salt is precipitated, the formula of which is  $\text{K}_3\text{Co}(\text{NO}_2)_6$ . It is known as potassium cobaltinitrite, or Fischer's salt, and its formation is employed as a test both for cobalt and for potassium. Nickel does not form an insoluble compound under the above conditions, so that the reaction is used to separate nickel and cobalt from each other.

**Cobaltamines.** When a salt of cobalt is treated with ammonia, the blue hydroxide  $\text{Co}(\text{OH})_2$  is at first precipitated. This dissolves in excess of ammonia, absorbs oxygen from the air, and is oxidized to the tervalent state. From solutions prepared in this way highly colored complex salts

are obtained, the composition of which depends upon the salt of cobalt used, other compounds which may be present, and the conditions of the experiment. As a class these salts are called the *cobaltammines*, and a great number of them have been prepared. The best-known type is represented by the formula  $\text{Co}(\text{NH}_3)_6\text{Cl}_2$ , which is named hexammino-cobaltichloride. These compounds have many interesting peculiarities, but a study of them would take us too far.

### NICKEL

**Occurrence and production.** The early metallurgists were acquainted with certain minerals of high metallic luster which strongly resembled the ores of copper, but from which they could not extract that metal, and which they accordingly named *kupfernickel*, or false copper. The labors of Cronstedt and Bergman in Sweden, toward the close of the eighteenth century, resulted in the isolation of the new metal and its clear differentiation from cobalt.

Nickel is almost always associated with cobalt in nature. Like the latter element, it occurs in combination with sulfur and arsenic and associated with copper, silver, and iron. Most of its ores are very complex, and it was formerly obtained, chiefly as a by-product, in the metallurgy of copper and silver. While there is probably more nickel than copper in the earth's crust, the production at present is confined largely to two centers, namely, the Sudbury district in Ontario, Canada, and the French island of New Caledonia. In the Sudbury district the nickel occurs in small amounts in the mineral *pyrrhotite* (a sulfide of iron) and is associated with chalcopyrite. Small amounts of platinum, palladium, and iridium are also present. The extraction of nickel from its ores is a complicated process and in brief is as follows:

The ore is smelted (that is, melted) in a blast furnace, and in this way there is obtained a mixture of the sulfides of iron, copper, and nickel. This mixture (or *matte*, as it is called) is heated in a Bessemer converter along with silica. The iron combines with the silica to form a slag which can be poured off. The resulting product consisting of the sulfides of nickel and copper and a little iron sulfide, is then melted with sodium sulfide which dissolves the copper and iron sulfides, leaving the nickel sulfide. This is then roasted and reduced with carbon.

**Properties and uses.** Nickel is a silvery metal capable of a very high polish. It is very hard, but is quite malleable. It can be welded on iron and the two rolled into sheets for making various kitchen utensils. Like iron and cobalt, it is magnetic. Its density is 8.9 and it melts at  $1452^{\circ}$ . It is not attacked by melted alkalis, and nickel crucibles are often employed in the laboratory for alkali fusions. The nonoxidizing acids evolve hydrogen with nickel very slowly, but nitric acid dissolves it readily.

The greatest use of nickel is in making nickel steels. While different steels may contain from 2 to nearly 50 per cent of nickel, those containing from 3 to 5 per cent are most suitable for ordinary commercial purposes. These steels are strong and tough and are widely used in the construction of different parts of machinery of various kinds, of large bridges, automobiles, locomotives, and cables. For military purposes they are used in armor plate, projectiles, and cartridges. An alloy of nickel and chromium has high electrical resistance and is used in electric heaters and furnaces. *Monel metal*, consisting of nickel, copper, and a small amount of manganese or iron, resists corrosion and has many uses. *Nickel coins* are made of an alloy of copper and nickel, while *German silver* contains zinc in addition. The pure metal is used in nickel-plating and for such purposes as making cooking utensils, spark-plug wires, and watch cases. In the form of a fine powder it is our most efficient catalyzer in reactions which consist in the union of hydrogen with some compound, as in hydrogenizing oils (p. 455).

**Oxides of nickel.** Nickel forms three well-known oxides of the formulas  $\text{NiO}$ ,  $\text{Ni}_2\text{O}_3$ , and  $\text{Ni}_3\text{O}_4$ , corresponding to those of iron and cobalt. Of these, nickelous oxide ( $\text{NiO}$ ) alone gives rise to a series of simple salts, corresponding to the ferrous salts. When anhydrous, these are usually yellow; and when hydrated, some shade of deep green. Only a few of these require description.

**Salts of nickel.** *Nickel sulfide* ( $\text{NiS}$ ), as prepared by precipitation, is a black, amorphous powder, insoluble in water and dilute acids, but easily soluble in more concentrated acids. *Nickel*

*chloride* ( $\text{NiCl}_2 \cdot 6 \text{H}_2\text{O}$ ), *nickel nitrate* ( $\text{Ni}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ ), and *nickel sulfate* ( $\text{NiSO}_4 \cdot 7 \text{H}_2\text{O}$ ) are the most familiar simple salts of this metal. The sulfate also forms crystals of the composition  $(\text{NH}_4)_2\text{SO}_4 \cdot \text{NiSO}_4 \cdot 6 \text{H}_2\text{O}$ , corresponding to Mohr's salt. It is the salt of nickel employed as the electrolyte in nickel plating, a piece of pure nickel being used as the anode and the object to be plated as the cathode. There are many complex salts of nickel.

**Nickel carbonyl ( $\text{Ni}(\text{CO})_4$ ).** When carbon monoxide is passed over metallic nickel at a temperature between  $30^\circ$  and  $50^\circ$ , the two unite to form a compound of the formula  $\text{Ni}(\text{CO})_4$ , known as nickel carbonyl. It is a colorless liquid, boiling at  $43.2^\circ$  and freezing at  $-25^\circ$  to colorless, needle-shaped crystals. When the vapor of the compound is passed through a tube heated to above  $100^\circ$ , the compound dissociates into the metal and carbon monoxide. Advantage is taken of this reaction in the Mond process for purifying nickel.

**Carbonyls of other metals.** Cobalt forms two carbonyls,  $\text{Co}(\text{CO})_8$  and  $\text{Co}(\text{CO})_4$ , but both of these are solids and are formed only under pressure. Iron forms three,  $\text{Fe}(\text{CO})_5$ ,  $\text{Fe}(\text{CO})_4$ , and  $\text{Fe}_3(\text{CO})_{12}$ . Of these the pentacarbonyl is a yellow liquid boiling at  $103^\circ$ . It sometimes forms in gas pipes and, upon its combustion, clogs the burner with iron oxide or injures the gas mantle by a deposit upon it.

## ARBITRARY RULES FOR BALANCING EQUATIONS

**Statement of rules.** For the purpose of balancing equations without knowledge of intermediate steps of the reaction, a certain number of arbitrary rules may be followed. These apply especially well to reactions of oxidation and reduction. The rules may be stated thus:

1. The valence of oxygen in any compound is always 2, and is considered as *negative* ( $-$ ). Thus, in  $\text{H}_2\text{O}$  we have  $-2$  valences for oxygen and in  $\text{H}_2\text{SO}_4$ ,  $4 \times 2 = -8$  valences for oxygen.

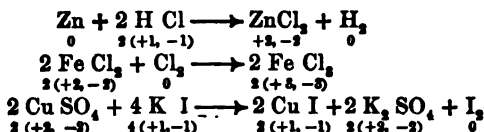
2. The valence of hydrogen in a compound, as well as the valences of metals that replace hydrogen from acids, is regarded as *positive* ( $+$ ), that of hydrogen being  $+1$ ,  $\text{Zn} = +2$ , and  $\text{Al} = +3$  (in salts).

3. The valence of a third element in a ternary compound is determined from the other two elements, the sum of the ( $+$ ) and ( $-$ ) valences in a compound being zero. Thus, in  $\text{H}_2\text{SO}_4$  we have  $\text{H} = +2$ ;  $\text{O} = 2 \times 4 = -8$ ; therefore  $\text{S} = +6$ . In  $\text{KClO}_3$  we have  $\text{K} = +1$ ;  $\text{O} = -6$ ; hence  $\text{Cl} = +5$ .

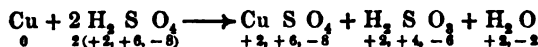
4. The valence of a free element as  $\text{Zn}$ ,  $\text{Cl}_2$ ,  $\text{N}_2$ , is zero, since no other element is held in combination.

5. In all chemical equations, on each side of the arrow the sum of negative valences equals the sum of the positive valences.

**Simple illustrations.** A few equations will illustrate these rules.



Since the radical  $\text{SO}_4$  does not change, it may be regarded as  $-2$  in valence. If the radical undergoes change, the valence of oxygen and sulfur must be considered separately, thus:

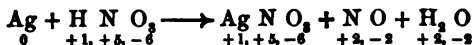


**Balancing an equation.** In balancing an equation the following steps should be followed:

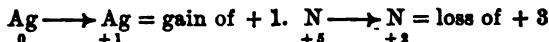
1. Set down the formulas of the materials used up and those formed, thus:



2. Write in the valence numbers where changes occur:



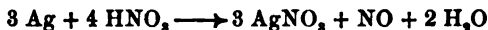
3. Note the extent of change in valence of each changing element:



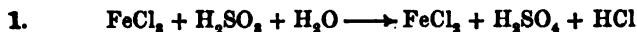
4. Supply coefficients of such kind as to make the loss balance the gain. The change in the N equals the change in 3 Ag, so the coefficients in the finished equation will be 3 Ag and 1  $\text{HNO}_3$ :



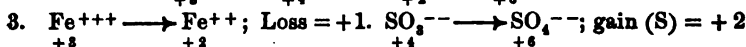
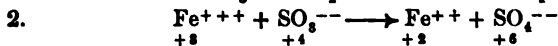
5. Complete the equation by adding those molecules not involving valence changes, but necessary to balance, namely, 3  $\text{HNO}_3$  on one side and 2  $\text{H}_2\text{O}$  on the other. This gives the finished equation:



**Balancing ionic equations.** In a similar way we may balance an equation on the basis of changes in the electrical charge on the ions concerned. In deducing the valences of the elements constituting a radical acting as an ion, however, we must make allowance for the charge on the ion, remembering that this charge always represents a valence balanced by some other ion in the solution, and of opposite sign. As an example let us deduce the equation representing the reduction of a solution of ferrous chloride by sulfurous acid, and let us follow the steps as indicated in the preceding illustration.

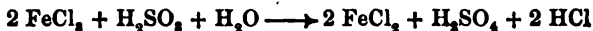


Or, on the basis of the ions undergoing change:



4. 2 Fe will be reduced by 1  $\text{SO}_4$ , giving the coefficients: 2  $\text{Fe}^{+++}$ , 1  $\text{SO}_4^{--}$ .

5. Supplying the unchanging ions, and water which takes a part but whose constituent atoms do not change valence:



### QUESTIONS

1. Suggest a reason why the metals so far studied do not occur free in nature.

2. How could you tell whether a given sample of iron was cast iron, wrought iron, or steel?

3. How could you prepare ferric chloride from copperas?

4. Is the reaction involved in the preparation of potassium ferri-cyanide from potassium ferrocyanide an oxidation or a reduction?

5. Write the equation for the reactions involved in the preparation of the following compounds from iron: ferrous sulfate, ferrous chloride, ferric sulfate, ferric chloride.

6. Explain how it is possible to use compounds of iron ( $\text{K}_4\text{Fe}(\text{CN})_6$ ) and ( $\text{K}_3\text{Fe}(\text{CN})_6$ ) in testing for the presence of iron in compounds.

7. Would you expect a solution of ferrous sulfate to react acid, basic, or neutral?

8. Write the equation for the reaction that takes place when pyrite is roasted in the air to obtain sulfur dioxide used in the manufacture of sulfuric acid.

9. Suppose you wish to reduce ferric chloride to ferrous chloride, how can you tell when the reduction is complete?

### PROBLEMS

1. Which of the ores of iron are richest in iron?

2. The iron ore from a certain mine is hematite, 90 per cent pure. Approximately what weight of steel containing 1 per cent of carbon can be prepared from 1000 tons of this ore, assuming that 10 per cent of iron is lost in the process?

3. A sulfuric acid plant has a daily output of 100 tons of acid containing 50 per cent of hydrogen sulfate. What weight of pyrite is required daily to furnish the necessary sulfur dioxide, assuming that the ore is 95 per cent pure and that 5 per cent of the sulfur is lost in the process?

4. What weight of pyrite is necessary for the preparation of 1000 kg. of Venetian red?

5. What weight of potassium ferricyanide will 10 kg. of crystalline potassium ferrocyanide yield?

6. What weight of nickel is necessary for the preparation of 100 g. of the hydrated nickel nitrate?

## CHAPTER XXXIX

### COPPER, MERCURY, AND SILVER

NAME	SYMBOL	ATOMIC WEIGHT	DENSITY	MELTING POINT	FORMULAS OF OXIDES	
					-ous	-ic
Copper . . . . .	Cu	63.57	8.93	1083.00°	Cu <sub>2</sub> O	CuO
Mercury . . . . .	Hg	200.60	13.56	- 38.87°	Hg <sub>2</sub> O	HgO
Silver . . . . .	Ag	107.88	10.50	960.50°	Ag <sub>2</sub> O	

**General.** Although these three elements do not form a periodic family, copper and silver belonging to one family and mercury to another, they have much in common, and it is convenient to describe them together. They are the first metals to be described that fall below hydrogen in the electrochemical series and do not liberate hydrogen from acids and water. They differ from the other metals already described in that they are found free in nature. Silver is univalent and forms but one series of salts. Copper and mercury form two series of salts, in which the metals are univalent and bivalent respectively.

#### COPPER

**Occurrence.** Metallic copper has been known from the earliest times and was probably the first metal to come into any considerable use. This is explained by its native occurrence and by the ease with which its oxygen compounds are reduced. It owes its name (from the Latin word *cuprum*) to the fact that the Romans obtained it from the island of Cyprus.

Large quantities of native copper, in a state approximating purity, are found in the northern peninsula of Michigan.

Smaller deposits are also found in a number of other localities. In combination it is found in a wide variety of forms, especially as sulfides, oxides, carbonates, and silicates. In small quantities it is present in the great majority of sulfide minerals, and in traces it is very widely distributed in nature. To some extent it is absorbed by plants growing in copper-bearing regions, and it is assimilated by some animals, as is shown by the fact that it occurs in the blood of the cuttlefish and in the feathers of some birds.

**Ores of copper.** The table which follows gives a list of the most important ores, chalcopyrite being by far the most valuable. Much copper is also produced from impure native copper.

SULFIDE ORES	OXYGEN ORES
Chalcopyrite . . . . . $\text{CuFeS}_2$	Cuprite . . . . . $\text{Cu}_2\text{O}$
Chalcocite . . . . . $\text{Cu}_2\text{S}$	Melaconite . . . . $\text{CuO}$
Bornite . . . . . $\text{Cu}_5\text{FeS}_4$	Malachite . . . . $\text{CuCO}_3 \cdot \text{Cu(OH)}_2$

The most important copper-producing regions in the United States are Arizona, Montana, Utah, and Michigan. Nearly all civilized countries produce some copper, but the United States produces more than one half of the world's supply. Enormous deposits that promise in time to make that country the leading copper-producing nation of the world have been opened up in Chile.

**Metallurgy.** Two general methods are used to separate copper from its ores:

1. *Leaching method.* This method consists in treating the ore with some reagent, such as dilute sulfuric acid or ammonium hydroxide, that will dissolve the copper. The metal is then separated from the solution by electrolysis. This method is, of course, only applicable when the copper is present in a form, such as the carbonate or oxide, which is soluble in the reagent employed.

2. *Smelting or pyro-metallurgical method.* This is the more important of the two methods. The copper ore, usually in the form of sulfides mixed or combined with other metallic sulfides, especially iron, as well as with small amounts of gold and silver, is heated with an appropriate flux in a

blast furnace or reverberatory furnace. The sulfides of copper and iron melt and the resulting liquid (known as *matte*) is separated from the slag, and is run into specially designed Bessemer converters. Any gold and silver present in the original ore is in solution in the liquid matte. Silica is now added and air is forced through the converter. The sulfides are changed to oxides by the process. The iron oxide combines with the silica, forming a slag that can be poured off, while the copper oxide reacts with some unchanged copper sulfide, as follows:



The resulting copper, which contains any gold or silver present in the ore, is run into molds and in this form is known as *blister copper*. This generally contains about 3 per cent of impurities, and is refined by electrolysis.

**Refining of copper.** Many of the uses for which copper is employed require a very pure metal, and for these purposes blister copper must be refined. This is accomplished by electrolysis.

The copper from the converter is cast into anode plates weighing upwards of 300 pounds. These are suspended in tanks containing a solution of copper sulfate as electrolyte, each anode plate being arranged opposite to a cathode made of a thin sheet of pure copper. The current, in passing through the cell, dissolves copper from the anode and deposits it upon the cathode in very pure form, the insoluble impurities collecting on the bottom of the tank as a mud. The cathode copper, while pure, is porous and is melted and cast into compact ingots. The electrolytic mud contains the gold and silver which was in the blister copper and is worked over to obtain these precious metals. It often contains tellurium as well, which at present has no commercial value.

**Flotation method for concentrating ores.** This method is a novel one recently introduced for concentrating ores, especially sulfide ores, not only of copper but of other metals as well. The ore is very finely pulverized and run into large tanks. Water, together with a small amount of pine oil (or some similar oil) is added to the ore and thoroughly mixed through it, either by stirring devices or by forcing compressed air through the mass. The oil, or the froth formed by blowing the air through the liquid, forms an envelope about the ore particles but not about the impurities. The froth rises to the surface of the water carrying the particles of ore, which can then be separated.

**Properties of copper.** Copper is a heavy metal of characteristic ruddy color, whose density averages about 8.93. It melts at 1083° and boils at 2310°. It is rather soft and is very

ductile, malleable, and flexible, yet tough and fairly strong. As an electrical conductor it is second only to silver. Its properties, notably its electrical conductivity, are much altered by impurities, especially by the presence of oxides and sulfides. It is not attacked by nonoxidizing acids, unless oxygen is present, nor by fused alkalies, but oxidizing acids convert it into the corresponding salts. In the presence of air most acids slowly act upon it; even carbon dioxide in moist air gradually covers its surface with a greenish coating of a basic carbonate. When heated in the air, it is oxidized to black copper oxide ( $\text{CuO}$ ). Sulfur and the halogens attack it with much more energy than does oxygen.

**Uses of copper.** Copper is extensively used in electrical construction, as a constituent of alloys, for roofing, for sheathing the bottoms of ships, for coinage, and for many minor purposes. The following table gives the names and approximate composition of some of its most important alloys.

Aluminium bronze . . . . .	90-98% copper, 2-10% aluminium
Brass . . . . .	63-73% copper, 27-37% zinc
Bronze . . . . .	70-95% copper, 1-25% zinc, 1-18% tin
German silver . . . . .	56-60% copper, 20% zinc, 20-30% nickel
Gun metal . . . . .	90% copper, 10% tin
Gold coin . . . . .	10% copper, 90% gold
Silver coin . . . . .	10% copper, 90% silver
Nickel coin . . . . .	75% copper, 25% nickel

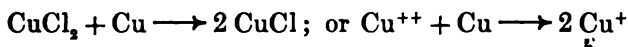
**Electrotyping.** Books are often printed from electrotype plates, which are prepared as follows: The face of the type is covered with wax, and this is firmly pressed down until a clear impression is obtained. The impressed side of the wax is coated with graphite, and this is made the cathode in an electrolytic cell containing a copper salt in solution. The copper is deposited as a thin sheet upon the letters in wax and, when detached, is a perfect copy of the type, the under part of the letters being hollow. The sheet is strengthened by pouring on the under surface a suitable amount of commercial lead. The sheet so strengthened is then used in printing.

**Simple compounds of copper.** Copper forms two series of simple salts derived from the oxides  $\text{Cu}_2\text{O}$  and  $\text{CuO}$ , known respectively as the *cuprous salts* and the *cupric salts*. Under

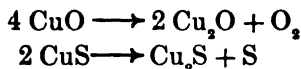
ordinary conditions, in the presence of moisture and air, the cupric salts are much the more stable, while at high temperatures the cuprous salts are the stable form. In aqueous solutions cupric compounds are blue, while cuprous compounds are colorless. Both cuprous hydroxide ( $\text{CuOH}$ ) and cupric hydroxide ( $\text{Cu}(\text{OH})_2$ ) are rather weak bases, and their salts are somewhat hydrolyzed in solution, giving the solution an acid reaction. They also form many basic salts, which are very sparingly soluble. All copper salts are more or less poisonous, especially to lower forms of life, and a number of them are used as insecticides. Copper and its salts have a catalytic action in a great many chemical reactions.

**Cuprous compounds.** Simple cuprous salts are rarely derived from oxygen acids, but are represented by such compounds as the oxide, sulfide, cyanide, and the halides. They are prepared in two general ways:

1. *By heating a solution of a cupric salt with a reducing agent.* The simplest reactions of this kind are those in which metallic copper is employed as the reducing agent. The preparation of cuprous chloride is an example:

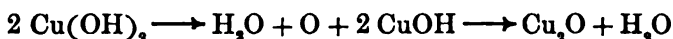


2. *By the dissociation of cupric compounds.* At higher temperatures most binary cupric compounds dissociate to form cuprous compounds:



Cuprous compounds are nearly all very sparingly soluble in water and are strong reducing agents tending to pass into cupric salts.

**Cuprous oxide ( $\text{Cu}_2\text{O}$ ).** Cuprous oxide is found in nature as a deep red mineral called *ruby copper*, or *cuprite*. It is formed as a precipitate when cupric compounds are heated with a reducing agent in alkaline solution. Cupric hydroxide is first formed, and this is then reduced as follows:

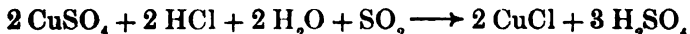


Certain sugars in solution effect this reduction, and the formation of cuprous oxide is often employed as a test for these. The oxide is used to impart a ruby red color to glass.

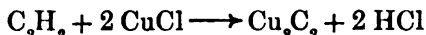
**Cuprous sulfide ( $\text{Cu}_2\text{S}$ ).** This compound is found in nature as a dark gray mineral called *chalcocite*. It is formed when cupric sulfide is heated in the absence of air, preferably in a current of hydrogen:

$$2 \text{CuS} + \text{H}_2 \longrightarrow \text{Cu}_2\text{S} + \text{H}_2\text{S}$$

**Cuprous chloride ( $\text{CuCl}$ ).** Cuprous chloride is a snow-white, crystalline solid, almost insoluble in water. It is most easily prepared by heating a solution of cupric chloride with copper turnings, or by passing a current of sulfur dioxide into a hot solution of a cupric salt and hydrochloric acid:



While practically insoluble in water, it is readily soluble in concentrated hydrochloric acid and in ammonia water, in both cases forming complex compounds. These solutions absorb many gases, especially oxygen, carbon monoxide, and acetylene. With acetylene a chocolate-colored precipitate of cuprous acetylide is thrown down:

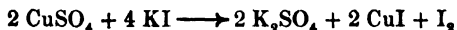


With carbon monoxide an addition product is formed:



The common method used for determining the percentages of these two gases present in gas mixtures is based upon these reactions.

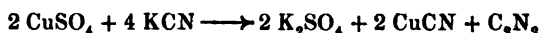
**Cuprous bromide ( $\text{CuBr}$ ) and cuprous iodide ( $\text{CuI}$ ).** These compounds have properties quite similar to those of the chloride, but they are more readily formed from the corresponding cupric salts. In the case of the iodide it is not necessary to employ a reducing agent, since cupric iodide spontaneously decomposes into the cuprous salt and free iodine. Being insoluble, it precipitates when a solution of an iodide is added to any simple cupric salt:



Since iodine can be very accurately estimated by means of sodium thiosulfate (p. 534), the quantity of copper present in a solution can be determined

with precision by measuring the iodine set free, and this reaction is much used in the commercial estimation of copper.

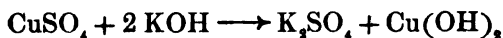
**Cuprous cyanide (CuCN).** This white, insoluble salt is formed by a reaction analogous to the one in which cuprous iodide is obtained, since cupric cyanide spontaneously decomposes into the cuprous salt and cyanogen:



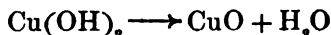
**Cupric salts.** The cupric salts are the familiar salts of copper. In most cases they are obtained by the usual methods, and a great variety of them are known, both normal and basic. In the solid state they are usually blue, green, or yellow; in dilute solution they are all blue. Some of them can be employed as mild oxidizing agents, being converted into cuprous compounds. Only a few require detailed description.

**Cupric oxide (CuO).** The black oxide of copper is usually obtained commercially by heating copper powder or turnings in the air. It is insoluble in water, but is readily soluble in acids, yielding the corresponding salts. Owing to the ease with which it gives up its oxygen, it is a good oxidizing agent and finds extensive use in the laboratory for such operations as the quantitative oxidation of carbon compounds. Industrially it is used on a large scale in the refining of petroleum for the removal of sulfur from the oil. It is regenerated from the resulting sulfur compounds by roasting in air, and is used over again.

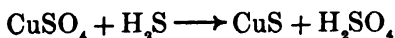
**Cupric hydroxide (Cu(OH)<sub>2</sub>).** The insoluble hydroxide results as a pale blue colloidal precipitate when any cupric salt is brought together with a solution of a metallic base:



When the mixture is heated, the hydroxide is converted into oxide:

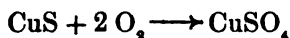


**Cupric sulfide (CuS).** Cupric sulfide results as a brownish-black precipitate when a solution of a cupric salt is treated with hydrogen sulfide:



It is insoluble both in water and in dilute acids. It is also nearly insoluble in a solution of ammonium sulfide, which distinguishes it from some other sulfides.

**Cupric sulfate ( $\text{CuSO}_4$ ).** In its industrial uses cupric sulfate is the most important of the salts of copper. Under ordinary conditions it crystallizes from solution in blue triclinic crystals, often of very large size, having the composition  $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$  and known as *blue vitriol*, or bluestone. A number of other hydrates are known, all of which, when strongly heated, yield the anhydrous salt, which is white. In the industries it is obtained in the refining of silver (p. 658) and by the oxidation of pyrite containing copper:



Prepared in these ways it contains a considerable percentage of ferrous sulfate as an impurity. It is used as a source of copper in the manufacture of other copper salts, as an electrolyte in copper refining, in electrotyping, and in batteries, and for the treatment of hoof diseases, particularly in sheep. A solution containing cupric sulfate, potassium sodium tartrate, and sodium hydroxide is known as *Fehling's solution* and is used in the determination of certain sugars (p. 644). The insecticide known as *Bordeaux mixture* is made by adding calcium hydroxide to a cold solution of copper sulfate. Many lower organisms, particularly those known as algae, are destroyed by even very small traces of soluble copper salts, and copper sulfate is sometimes added to the water supply of cities to kill the algae, whose growth imparts an unpleasant taste and odor to the water.

**Cupric carbonate.** The normal carbonate of copper is not known, but there are a number of basic carbonates, the chief of which are  $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$  and  $2 \text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ . Both of these occur in nature, the former as the green mineral *malachite* and the latter as the blue mineral *azurite*. The green color of weathered copper is due to the formation of basic carbonates.

**Other cupric salts.** Among the other cupric salts frequently used in the laboratory are the following, most of which form other hydrates in addition to those given:

Cupric nitrate ( $\text{Cu}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ ), blue, deliquescent crystals.

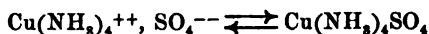
Cupric chloride ( $\text{CuCl}_2 \cdot 2 \text{H}_2\text{O}$ ), light blue, pearly scales, or needles.

Cupric bromide ( $\text{CuBr}_2$ ), brownish-purple crystals resembling iodine.

Cupric acetate ( $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{H}_2\text{O}$ ), a blue, easily crystallized salt.

**Complex salts of copper.** Like nearly all the metals of high density, copper forms a great many double and complex salts, a study of which would take us too far. Only two general classes will be mentioned here; these are of importance in themselves and represent classes which will frequently recur with other metals.

1. **Ammonia compounds.** When cupric sulfate is treated with aqua ammonia, the insoluble hydroxide is at first precipitated, as would be expected. Continued addition of ammonia causes the precipitate to dissolve, forming an intensely blue-purple solution. From this solution, under favorable conditions, there crystallizes a solid of the same intense color, which has the formula  $\text{Cu}(\text{NH}_3)_4\text{SO}_4 \cdot \text{H}_2\text{O}$ . The great majority of cupric salts yield similar compounds with excess of ammonia, and all have the same intense color, quite unlike the pale blue of simple copper salts. The copper ion of copper hydroxide combines with ammonia to form the complex ion  $\text{Cu}(\text{NH}_3)_4^{++}$ , which remains in equilibrium with the sulfate ion  $\text{SO}_4^{--}$ .

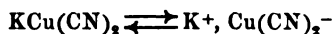


Salts of this kind containing ammonia molecules as a constituent of the cation are called *ammino-salts*, the salt just described being *tetrammino-cupric sulfate*. The dissolving of a precipitate by continued addition of the reagent which produced it may usually be taken to indicate the formation of a complex ion of this general kind.

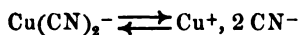
Under similar circumstances cuprous compounds yield colorless compounds in which there are usually two ammonia groups. Thus, diammino-cuprous chloride has the formula  $\text{Cu}(\text{NH}_3)_2\text{Cl}$ .

2. **Complex cyanides.** We have seen that when a cupric salt and a soluble cyanide are brought together in solution, insoluble cuprous cyanide ( $\text{CuCN}$ ) is formed. If an excess of the cyanide is added, the precipitate dissolves, and the resulting solution is colorless. When treated with the reagents which usually precipitate copper compounds (for example, with hydrogen sulfide) it gives no precipitate, nor does it turn blue-purple with ammonia. These facts point to the formation of a complex ion, and experiment shows that the product is a complex cyanide. Several different cyanides may form,

depending upon conditions, a typical one having the formula  $\text{KCu}(\text{CN})_2$ . This compound ionizes as shown in the equation



The copper has become a part of a complex anion, and only to an extremely limited extent are simple cuprous ions formed by a secondary ionization:



**Electric cells.** An electric cell is a device for converting chemical energy directly into electrical energy. A great many different chemical reactions can be arranged in such a way as to accomplish this result, and the combination known as the *Daniell cell* will serve as an illustration of the most familiar types of cells. In this combination two plates, one of copper and the other of zinc, each fashioned so as to have a large surface, are arranged in a glass jar, as shown in Fig. 172. The electrolyte in contact with the zinc plate is zinc sulfate, while that in contact with the copper plate is copper sulfate.

**Action of the Daniell cell.** The action of the cell can be explained as follows: The zinc atoms have a tendency to give up to the zinc plate

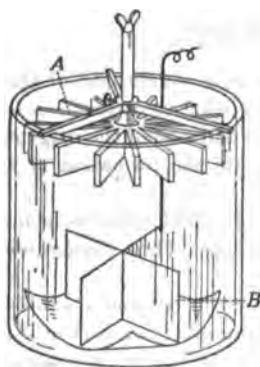
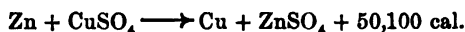


FIG. 172

two electrons each, and to pass into solution as zinc ions, the force urging this change being designated as *solution tension*. But since the zinc ions are positively charged, and their formation leaves the zinc plate negatively charged, the accumulation of these charges soon produces an equilibrium by the attraction of the zinc plate for the positive ions. Copper ions, on the other hand, tend to leave the solution because of their *osmotic pressure*, and to deposit as metallic atoms upon the copper plate B, each copper ion recovering two electrons from the copper plate. Since this process results in charging the copper plate positively, the accumulated charge soon produces an equilibrium by repelling the posi-

tive copper ions. If now the two plates are joined by a wire, the excess electrons on the zinc plate flow through the wire to make up the deficiency upon the copper plate. This prevents an accumulated charge on either

plate and results in a current through the wire. The chemical action taking place is represented by the equation



in which nearly all the heat is transformed into electrical energy. The reaction ceases when the wire connection is broken.

The order of the metals in the electrochemical series (p. 245) is the order of intensity with which the metals tend to pass into ionic form. Any two metals in a suitable electrolyte will constitute a cell in which the metal highest in the series is the negative pole and the lower one the positive. As a rule, only a part of the chemical energy is converted into electrical energy, the remainder being transformed into heat.

### MERCURY

**History and occurrence.** The element mercury, or *quicksilver* as it is often called, was known considerably before the Christian era and played an important part in the alchemy of the Middle Ages. It is found in a number of localities, usually in the form of a red sulfide called *cinnabar* and occasionally as drops of native metal. As a rule, the ores are not very rich, in many cases carrying less than 1 per cent of mercury. In the order of their present production, Spain, California, and Austria produce the most mercury.

**Metallurgy.** The metallurgy of mercury is extremely simple, owing to the ready decomposition of its compounds and the volatility of the metal. It is only necessary to roast the sulfide in a current of air:  $\text{HgS} + \text{O}_2 \longrightarrow \text{SO}_2 + \text{Hg}$

The resulting vapor of mercury is easily condensed to a liquid.

**Purification of mercury.** Solid materials mixed with mercury are removed by filtration through soft leather. The impurities remaining are chiefly other metals held in solution. With few exceptions these are more easily oxidized than mercury and may be removed by digesting the mercury with a solution of an oxidizing agent, such as nitric acid or ferric chloride.

**Laboratory purification.** In the laboratory it is often necessary to prepare pure mercury for various purposes, and this may be accomplished conveniently by the apparatus shown in Fig. 173. A long glass tube A,

drawn out to an S-shaped trap *B* at the lower end, is filled with enough mercury to close the trap and is then filled up with a solution of ferric chloride. The end of the funnel *C* is drawn to a fine tip through which the mercury streams, falling through the ferric chloride solution in a fine spray and overflowing at the bottom into a receiving vessel *D*. For very refined purposes it is better to distill the mercury under diminished pressure, though Hulett has shown that the presence of a little oxygen is preferable to a complete vacuum, insuring the oxidation of the metallic impurities and preventing their volatilization along with the mercury.

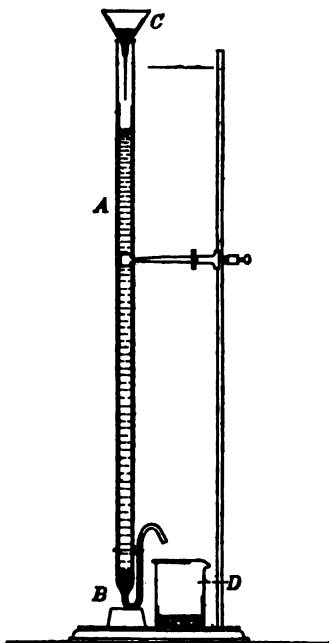


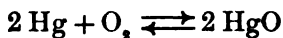
FIG. 173

**Properties.** Pure mercury is a silvery liquid at ordinary temperatures, and to this fact it owes the name *quicksilver* (the word *quick* meaning "live," or "moving"). It solidifies at  $-38.87^{\circ}$ , boils at  $357^{\circ}$ , and at  $15^{\circ}$  has a density of 13.56. Its various properties give it great value in scientific experi-

mentation. It is a convenient liquid over which to collect gases that are soluble in water. It has a moderately large coefficient of expansion with temperature changes, and this fact, together with its low freezing point and fairly high boiling point, renders it suitable for use in the construction of thermometers. Its density and low vapor pressure at ordinary temperatures make it a convenient liquid for barometers, since a column less than one meter in height will balance the atmospheric pressure, with all its range of variation. It is a moderately good conductor of electricity and therefore affords a convenient means of joining conducting wires in cases where rigid joints would be inconvenient.

It forms alloys (called *amalgams*) with practically all the metals. This property leads to the largest industrial use of the metal, namely, in the extraction of gold and silver from their ores. When little of the other metal is present, the amalgams are liquid but not so mobile as pure mercury and inclined to be stringy. Some of these amalgams have industrial uses. Sodium amalgam in contact with water is an efficient reducing agent.

**Chemical conduct.** Mercury is a metal of rather feeble chemical activity. It stands low in the electrochemical series and is thrown out of combination by most other metals. Heated in the air at temperatures below its boiling point, it slowly combines with oxygen to form the red oxide, but this is easily decomposed at higher temperatures, the reaction being reversible:



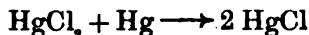
It does not displace hydrogen from acids, but oxidizing acids attack it, forming the corresponding salts. As with copper, it has a greater tendency to combine with sulfur and the halogen elements than with oxygen.

**Salts of mercury.** Like copper, mercury forms two series of compounds — the *mercurous* and the *mercuric*. The general stability of the two series is much more nearly equal than is the case with copper salts, and salts of the oxygen acids, as well as of practically all other acids, are known in each series. The salts of mercury are remarkable for the fact that, compared with other salts, they are very little ionized in solution. For example, a normal solution of mercuric chloride at ordinary temperatures is ionized to an extent of less than 0.01 per cent. The salts of mercury are also much more generally soluble in organic solvents, such as alcohol and ether, than is usually the case with metallic salts. Both the metal and its salts are poisonous. Nearly all compounds of mercury dissociate at high temperatures, yielding free mercury.

**Mercurous salts.** Mercurous salts are obtained in either of two general ways.

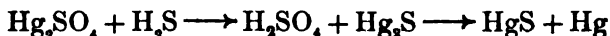
1. *By precipitation.* The insoluble salts can be obtained by double decomposition with soluble mercurous salts, such as the nitrate  $\text{HgNO}_2$ :  $\text{HgNO}_2 + \text{NaBr} \longrightarrow \text{HgBr} + \text{NaNO}_2$ .

2. *By reduction of a mercuric salt.* This is most conveniently effected by the use of mercury as a reducing agent. Thus mercuric chloride, when heated with mercury, yields mercurous chloride:

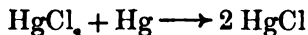


When mercury is dissolved in cold, dilute oxidizing acids, the mercurous salt is obtained if mercury is in excess, for any mercuric salt which may be formed is then reduced.

**Mercurous oxide ( $\text{Hg}_2\text{O}$ ); hydroxide ( $\text{HgOH}$ ); sulfide ( $\text{Hg}_2\text{S}$ ).** All of these insoluble compounds are apparently formed by the usual methods of preparation, but they are very unstable and quickly decompose into the more stable mercuric compounds, especially under the influence of sunlight. The preparation and decomposition are illustrated in the equation for the sulfide:



**Mercurous halides.** The mercurous halogen compounds are comparatively stable and well characterized, the iodide being the least so. They are insoluble in water. The chloride  $\text{HgCl}$ , known as *calomel*, is prepared by subliming mercuric chloride with mercury:



It is also prepared by subliming mercurous sulfate with common salt. It is a white, crystalline body, easily volatile, and has important uses as a drug. In strong sunlight the reaction just given is to some extent reversed, the preparation darkening in consequence of the separation of mercury. Since the mercuric chloride formed at the same time is exceedingly poisonous, it is necessary to preserve calomel in dark bottles. The bromide  $\text{HgBr}$  and the iodide  $\text{HgI}$  have similar properties. They decompose with ease, the iodide ranging in color from yellow to green, apparently through decomposition.

**Mercurous nitrate ( $\text{HgNO}_3$ ).** This salt is formed when cold dilute nitric acid acts upon mercury. It is quite soluble, forms monoclinic needles of the hydrate  $\text{HgNO}_3 \cdot 2\text{H}_2\text{O}$ , and undergoes hydrolysis in dilute solution, forming a basic salt.

**Mercurous sulfate ( $\text{Hg}_2\text{SO}_4$ ).** Mercurous sulfate is formed in a similar way by the action of sulfuric acid upon mercury. A very pure preparation may be made electrolytically by placing a suitable quantity of mercury in a beaker and pouring over it dilute sulfuric acid. An insulated wire is dipped into the mercury, which is made to serve as anode, while a small piece of platinum foil dipped into the acid serves as the cathode. When a suitable current is passed through the cell so formed, the mercury dissolves in the acid, forming mercurous sulfate. The mercury is gently stirred during solution to prevent the formation of the mercuric salt. The sulfate is somewhat hydrolyzed by water.

**Standard cells.** The chief use of mercurous sulfate is in the construction of standard cells. These are small cells which have a very constant electromotive force, against which other cells may be standardized. The arrangement most often used is represented in Fig. 174 and is called the *Weston cell*. Two small glass test tubes, through the bottom of each of which is sealed a platinum wire, are connected by a glass tube so as to form an H-shaped vessel. Mercury in contact with a paste of mercurous sulfate and water is placed in the one tube (*A*), while cadmium (in the form of amalgam) in contact with a saturated solution of cadmium sulfate, is placed in the other (*B*), the connecting tube being also filled with the latter solution. Crystals of cadmium sulfate are sometimes placed in each tube to insure the saturation of the solution. Such a cell has an electromotive force of 1.0186 volts at  $20^\circ$ .

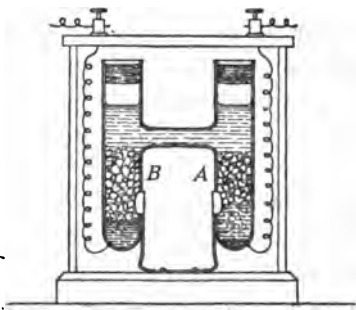


FIG. 174

**Mercuric salts.** Mercuric salts are usually prepared by oxidation of mercurous salts or by the solution of mercuric oxide or mercury in the appropriate acid. As a rule, they are more

soluble than the corresponding mercurous salts and are more extensively hydrolyzed in solution, yielding a great variety of basic salts, which are usually of some shade of yellow. They also yield many complex compounds.

**Mercuric oxide (HgO).** Mercuric oxide is prepared as a bright red, crystalline powder by the careful heating of mercuric nitrate. It is also obtained as a yellow precipitate when a cold solution of a soluble base is poured into a solution of a mercuric salt. The hydroxide, which would be expected to form in the reaction, spontaneously decomposes into oxide:



The yellow oxide changes into the red at a higher temperature, but it is not entirely certain whether these two are distinct forms or whether they owe their different colors to differences in their fineness of division. When the oxide is heated, it dissociates into mercury and oxygen — a reaction which led Priestley to the discovery of oxygen.

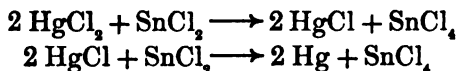
**Mercuric sulfide (cinnabar) (HgS).** Mercuric sulfide occurs in nature as the red mineral *cinnabar*, and is the most important natural compound of mercury. The compound can be obtained by precipitation, as shown in the following equation:



When it is so prepared, it is a black, amorphous substance, very highly insoluble in water and in acids. When mercury and sulfur are intimately ground together (forming the black, amorphous sulfide) and the product is warmed with a solution of potassium sulfide (in which mercuric sulfide is somewhat soluble), the bright red variety known as *vermilion* is obtained. It is a valuable pigment.

**Mercuric chloride (corrosive sublimate) (HgCl<sub>2</sub>).** Mercuric chloride can be obtained by the usual methods as a white, crystalline solid moderately soluble in water. In the industries it is made by heating a mixture of ordinary salt and mercuric sulfate,

and condensing the volatile chloride. It is soluble in alcohol and in ether, as well as in water, and is extensively used in surgery as an antiseptic. It is extremely poisonous. It combines directly with a great variety of substances, among others with albumin. This latter fact leads to the use of white of egg as an antidote for the compound, though no antidote is very effective. When treated with a reducing agent, it is easily reduced to mercurous chloride and often to free mercury. The reactions with stannous chloride, for example, are shown in the following equations:



**Mercuric iodide ( $\text{HgI}_2$ ).** This salt is interesting as occurring in two very different forms. At ordinary temperatures the stable form is bright scarlet in color. Above  $126.5^\circ$  this changes to a yellow modification which melts at  $223^\circ$ , and when cooled below  $126.5^\circ$  it changes again into the red form. It is very sparingly soluble in water, but dissolves readily in solutions of potassium iodide, forming the complex compound  $\text{K}_2\text{HgI}_4$ . This solution, with the addition of potassium hydroxide, is known as *Nessler's reagent*, and is used in detecting the presence of small traces of ammonia, especially in potable waters. The reactions will be described in a later paragraph (p. 657).

**Other mercuric salts.** A few other mercuric salts should be mentioned very briefly.

**Mercuric cyanide ( $\text{Hg}(\text{CN})_2$ )** is a white solid, easily decomposed by heat into mercury and cyanogen (p. 386).

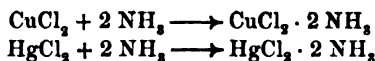
**Mercuric nitrate ( $\text{Hg}(\text{NO}_3)_2$ )** crystallizes from dilute nitric acid in the form of a hydrate of the composition  $\text{Hg}(\text{NO}_3)_2 \cdot 8 \text{H}_2\text{O}$ . In water it undergoes hydrolysis, with the formation of basic salts.

**Mercuric sulfate ( $\text{HgSO}_4$ )** is known both as the anhydrous salt and as the monohydrate  $\text{HgSO}_4 \cdot \text{H}_2\text{O}$ . Both salts are white, crystalline solids, which are hydrolyzed in the presence of much water, forming a yellow basic salt of the formula  $\text{HgSO}_4 \cdot 2 \text{HgO}$ , known as *turpeth*.

**Mercuric fulminate ( $\text{Hg}(\text{OCN})_2$ )** is prepared by the action of nitric acid upon mercury in the presence of alcohol. It is extremely explosive and is used in the manufacture of primers for cartridges.

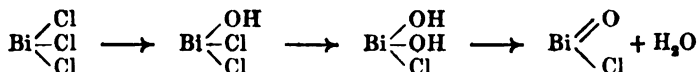
**Ammonia compounds of mercury.** Among the most numerous complex compounds of mercury are those which its salts form with ammonia. A large number of these compounds have been described, and have been extensively studied by Franklin. They can be understood most easily by remembering that liquid ammonia and water, as solvents, have many qualities in common, and that their reactions with salts are closely analogous. These compounds may then be grouped into three classes:

1. *Analogues of hydrates.* Just as a salt may take up water to form a hydrate, so it may combine with ammonia to form an *ammoniate*:

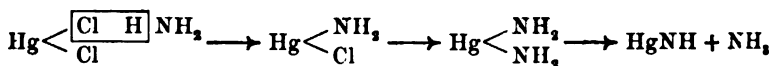


The ammoniate of calcium chloride ( $\text{CaCl}_2 \cdot 8 \text{NH}_3$ ) has been mentioned on an earlier page (p. 255).

2. *Analogues of basic salts.* The hydrolysis of salts has already been explained (p. 326) and is well illustrated in the case of bismuth chloride, in which the following stages occur:

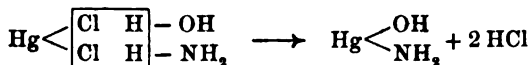


With mercuric salts there is a corresponding action which Franklin has aptly named *ammonolysis*. With the chloride the stages are



Compounds of this type, formed by ammonolysis and analogous to basic salts, are called *ammonia-basic salts*.

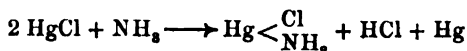
3. *Mixed types.* When mercury salts are treated with *aqueous ammonia*, which may be regarded as a mixed solvent consisting of water and ammonia, both *hydrolysis* and *ammonolysis* may occur. In the case of the chloride this is represented by the equation



The product of this reaction is both *water-basic* and *ammonia-basic*.

Reactions which can be referred to these types occur with most mercuric salts. With mercurous salts there is at the same time a decomposition

which results in the formation of a mercuric derivative and free mercury, as is illustrated in the case of calomel:



The ammonia-basic mercuric chloride formed in this reaction is a white compound, but it appears to be jet-black, owing to the finely divided mercury precipitated at the same time. Many of these compounds were known long before their nature was understood, and they have various accidental names. A few well-known ones are the following:

- $\text{HgCl}_2 \cdot 2 \text{NH}_3$ , fusible white precipitate (class 1)
- $\text{NH}_2 - \text{Hg} - \text{Cl}$ , infusible white precipitate (class 2)
- $\text{HO} - \text{Hg} - \text{NH} - \text{Hg} - \text{OH}$ , Millon's base (class 3)
- $\text{HO} - \text{Hg} - \text{NH} - \text{Hg} - \text{I}$ , Nessler's precipitate

This last compound is the iodide of Millon's base and is formed when mercuric chloride, potassium iodide, and ammonia are brought together in alkaline solution. It is a dark, reddish-brown precipitate, and even minute traces of ammonia will give a yellow coloration with these reagents (Nessler's solution, p. 655).

## SILVER

**History and occurrence.** Silver, the *argentum* of the Romans, has been known from the earliest times and, together with gold, has always ranked as a precious metal. It is frequently found native in the form of flakes or wire imbedded in primitive rock, and occasionally in large masses. In the combined state it occurs in many minerals, those of most importance to the metallurgist being the following: *cerargyrite* (horn silver) ( $\text{AgCl}$ ); *argentite* ( $\text{Ag}_2\text{S}$ ); *proustite* ( $\text{Ag}_3\text{AsS}_3$ ); *pyrargyrite* ( $\text{Ag}_3\text{SbS}_3$ ); *stephanite* ( $5 \text{Ag}_2\text{S} \cdot \text{Sb}_2\text{S}_3$ ). It is also found in small quantities in practically all copper and lead ores, a considerable quantity of the silver now produced coming from this source.

**Metallurgy.** In a text of this scope it is possible to explain only the most general principles of the metallurgy of silver, since the details are very complicated and subject to frequent change. The methods employed may be classified under three heads:

1. *Smelting.* In furnace smelting the ores are mixed with lead ores (if they are not already rich enough in lead), and the two metals are obtained as an alloy. The separation will be described in the following chapter.

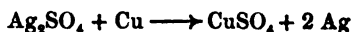
2. *Amalgamation.* When silver occurs native, or in forms which can be readily converted into metallic silver by suitable reagents, the ores, together with the reagents, are thoroughly mixed with mercury, which dissolves the silver and gold. The resulting amalgam is then collected and the mercury distilled off, leaving the impure silver.

3. *Hydrometallurgy.* In this process the silver is dissolved from the finely crushed ore by a solution of some suitable reagent. Sometimes sulfide ores are roasted until the silver is converted into sulfate, which is itself soluble in water. In other cases solutions of sodium cyanide, sodium mercurous cyanide ( $\text{NaHg}(\text{CN})_2$ ), or sodium thiosulfate are employed, all of which dissolve silver as well as some silver compounds. From the solution of silver so obtained the metal is precipitated by a suitable reagent such as copper, zinc, or sodium sulfide.

**Refining of silver.** There are a number of methods by which silver is refined, two of which may be mentioned.

1. *Cupellation and parting with sulfuric acid.* In this process the metal is heated on an open hearth in a strong current of air. The various metallic impurities (excepting gold) are in this way largely converted into oxides and swept off as *dross*, leaving the silver alloyed with small percentages of gold, copper, and iron. It is then cast into ingots known as *doré* bars, since they contain gold.

In order to recover the gold, the alloy is treated with hot concentrated sulfuric acid, which converts all the metals, except the gold, into sulfates. When water is added to the resulting mixture, the sulfates of copper, silver, and iron pass into solution, while the gold, together with any unattacked substances, settles as a mud from which the gold is subsequently recovered. The silver is separated from the solution of the sulfates by suspending in the latter clean copper plates, the copper displacing the silver, which is deposited in crystalline form:



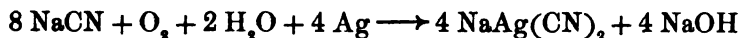
The copper sulfate obtained as a by-product in this process furnishes much of the blue vitriol of commerce.

2. *Electrolytic refining.* Electrolysis of the impure silver is now carried out extensively, the process being conducted in a way very similar to the electrolysis of copper. The electrolyte used is a solution of silver nitrate in nitric acid. The silver is deposited as crystals, which are mechanically brushed off the cathode, collected, and melted into bars.

The United States produces over one third of the world's output of silver, and the American continent, about 80 per cent.

**Properties.** Silver is a brilliant white metal which melts at 960.5°, boils at 1955°, and has a density of 10.5. It is very ductile and malleable and has the greatest electrical conductivity of any of the metals. It is intermediate in hardness between gold and copper, and in thin foil transmits blue light. It alloys with many other metals and dissolves readily in mercury, forming an amalgam. When melted it dissolves notable quantities of oxygen, giving it up again during solidification, with a characteristic sputtering of the metal. One gram of silver gives up about 1 cc. of oxygen. It crystallizes in octahedra, but much of the native silver is not notably crystalline. It can be obtained in colloidal suspension by sparking silver wires under water (p. 506) or by chemical reduction. It is extensively used for household ornaments and utensils, for coinage (p. 642), in the manufacture of mirrors, and as halogen salts in photography. Much of the output is exported each year to the Far East.

**Chemical conduct.** Silver is one of the inactive elements. It does not combine directly with oxygen, hydrogen, carbon, nitrogen, silicon, and other elements, nor is it acted upon by dilute acids or fused alkalis. The halogen elements attack it slowly and only superficially, since insoluble halides are formed which prevent further action. Ozone attacks it, forming a black peroxide. Sulfur, as well as most sulfur compounds, blackens it, owing to the formation of silver sulfide (oxidized silver). The oxidizing acids dissolve it, forming the corresponding salts, such as the nitrate  $\text{AgNO}_3$ , and the sulfate  $\text{Ag}_2\text{SO}_4$ . Sodium cyanide, in the presence of air and water, dissolves it according to the following equation :

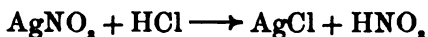


**Compounds of silver.** Silver forms only one well-defined series of salts, and in these it is univalent. These salts are usually colorless or light yellow, and are little hydrolyzed in solution, yielding few basic salts. They are readily reduced to metallic silver, and consequently are mild oxidizing agents. In addition

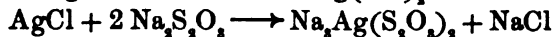
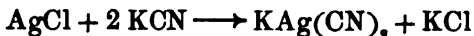
to these salts, there are a few compounds in which the valence is open to question and there are many complex salts. The salts of silver are characterized by the fact that very few of them form hydrates.

**Silver oxide ( $\text{Ag}_2\text{O}$ ).** Silver oxide is thrown down as a dark brown, amorphous precipitate when a soluble hydroxide is added to a solution of a silver salt, the hydroxide at first formed spontaneously decomposing into water and the oxide. It is sufficiently soluble in water to turn red litmus blue, evidently forming some hydroxide, and it acts as a strong, highly ionized base, yielding salts which are neutral to litmus. At a very moderate temperature it decomposes into silver and oxygen, the reaction being rapid at  $250^\circ$ .

**Silver halides.** Silver fluoride ( $\text{AgF}$ ) is prepared by dissolving silver oxide in hydrofluoric acid. It is a very soluble salt, crystallizing as the hydrate  $\text{AgF} \cdot \text{H}_2\text{O}$  or  $\text{AgF} \cdot 2 \text{H}_2\text{O}$ . The other halides, on the contrary, are practically insoluble, the chloride being the most soluble of the three and the iodide the least so. They are prepared by treating a soluble silver salt with either a soluble halide salt or the free acid:



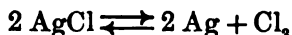
They form amorphous, curdy precipitates, the chloride being white, the bromide very pale yellow, the iodide decidedly yellow. All three are also known in crystalline condition. The formation of these precipitates is used as a test, on the one hand for silver ions and on the other for the halogen ions. The halides are soluble in a number of normal salts, forming a series of complexes. This property is of importance in metallurgy and in photography. A few of these reactions are shown in the following equations, silver chloride being used as an example:



The chloride is also soluble in ammonium hydroxide, forming the complex salt  $\text{Ag}(\text{NH}_3)_2\text{Cl}$ , which can be obtained in the

form of shining, colorless needles. With gaseous ammonia the chloride and iodide form the ammoniates  $2 \text{AgCl} \cdot 3 \text{NH}_3$ ,  $\text{AgCl} \cdot 3 \text{NH}_3$ , and  $\text{AgI} \cdot 2 \text{NH}_3$ .

All three of the insoluble silver halides are sensitive to light, darkening in color as the result of a change in which a portion of the halogen element is liberated. In the dark this reaction is reversed. While the nature of the change is not thoroughly understood, it seems probable that it is chiefly decomposition.



The reduced silver remains in colloidal dispersion in the colloidal silver chloride that escapes reduction. It is upon this property of these halides that the art of photography is based.

**Photography.** From a chemical standpoint the processes involved in photography may be described under two heads: (1) the preparation of the negative; (2) the preparation of the print.

1. *Preparation of the negative.* The plate used in the preparation of the negative is made by spreading a thin layer of gelatin, in which colloidal silver bromide is suspended (silver iodide is sometimes added also), over a glass plate or a film composed of nitrocellulose or cellulose acetate (p. 447) and allowing it to dry. When the plate so prepared is placed in a camera and the image of some object is focused upon it, the silver salt undergoes decomposition which is proportional at each point to the intensity of the light falling upon it. In this way an image of the object photographed is produced upon the plate, which is, however, invisible and is therefore called *latent*. It can be made visible by the process of developing.

To develop the image, the exposed plate is immersed in a solution of some reducing agent, called the *developer*. While the developer will in time reduce all the silver salt present, it acts much more rapidly upon that which has been exposed to the light. The plate is therefore left in contact with the developer only long enough to properly bring out the image. The resulting metallic silver is deposited in the form of a black film, which adheres closely to the plate.

The unaffected silver salt is then removed from the plate by immersing it in a solution of sodium thiosulfate. After the silver salt has been dissolved, the plate is washed with water and dried. The plate so prepared is called the *negative*, because it is a picture of the object photographed, with the lights exactly reversed.

2. *Preparation of the print.* The print is made from paper which is prepared in the same way as the negative plate. The negative is placed upon

this paper and exposed to the light in such a way that the light must pass through the negative before striking the paper. If the paper is coated with silver chloride, a visible image is produced, in which case a developer is not needed. It is in this way that proofs are made; in order to make them permanent, the unchanged silver chloride must be dissolved off with sodium thiosulfate. The print is then toned by dipping it into a solution of gold or platinum salts. The silver on the print passes into solution, while the gold or platinum takes its place. These metals give a characteristic color, or tone, to the print, the gold making it reddish brown, while the platinum gives it a steel-gray tone. If a silver bromide paper is used in making the print, a latent image is produced which must be developed, as in the case of the negative itself. The silver bromide is much more sensitive than the chloride, so that the printing can be done in artificial light. Since the darkest places on the negative cut off the most light, it is evident that the lights of the print will be the reverse of those of the negative, and will therefore correspond to those of the object photographed.

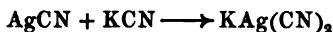
**Silver nitrate (lunar caustic) ( $\text{AgNO}_3$ ).** Silver nitrate is prepared by the action of nitric acid upon silver, and it is the salt of silver most extensively used in the laboratory. It is extremely soluble in water, 100 g. of solvent at  $20^\circ$  dissolving 215 g., and at  $100^\circ$ , 910 g. It crystallizes in colorless rhombic plates and melts undecomposed at  $208.6^\circ$ . It is often cast into sticks for use as a caustic in surgery, its use depending upon the fact that it is a powerful oxidizing agent. It produces a black stain on the skin, owing to a deposit of metallic silver. A similar stain is produced upon any other oxidizable material, such as cloth, and because of this fact silver nitrate is used in the manufacture of indelible inks. It dissolves in aqua ammonia, forming the ammino salt  $\text{Ag}(\text{NH}_3)_2\text{NO}_3$ .

**Other soluble salts.** Among the other soluble salts of silver the most important are the sulfate  $\text{Ag}_2\text{SO}_4$ , which is but sparingly soluble, and the acetate  $\text{AgC}_2\text{H}_3\text{O}_2$ , which crystallizes in shining needles. The nitrite  $\text{AgNO}_2$  is soluble in hot water.

**Insoluble salts.** In addition to the halogen compounds already described, many of the salts of silver are insoluble and have characteristic colors, or appearances, which serve to identify the various anions in analysis. Among these are the following:

*Silver sulfide* ( $\text{Ag}_2\text{S}$ ) is found in nature as *argentite* and, as prepared by precipitation, is a black, amorphous solid. It is the most insoluble of silver compounds both in water and in acids.

*Silver cyanide* ( $\text{AgCN}$ ) forms as a curdy white precipitate when a soluble cyanide is added to a silver salt. It is soluble in excess of the precipitant, forming a complex cyanide:



The following compounds are of less importance:

Silver carbonate ( $\text{Ag}_2\text{CO}_3$ ), a pale yellow powder.

Silver chromate ( $\text{Ag}_2\text{CrO}_4$ ), a brick-red, amorphous solid.

Silver phosphate ( $\text{Ag}_3\text{PO}_4$ ), a clear, yellow solid.

Silver pyrophosphate ( $\text{Ag}_4\text{P}_2\text{O}_7$ ), a granular, white powder.

**Electroplating.** Since silver has a pleasing appearance and is not acted upon by water or air, it is used to coat various articles made of cheaper metals. Such articles are said to be silver-plated. The process by which this is done is called

*electroplating* and is carried on as follows: The object to be plated (a spoon, for example) is attached to a wire and dipped into a solution of a silver salt. Electrical connection is made in such a way that the

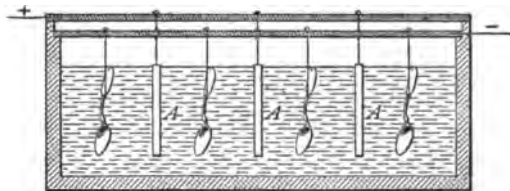


FIG. 175

article to be plated serves as a cathode, while the anode is made up of one or more plates of silver (Fig. 175, A). When a current is passed through the electrolyte, silver dissolves from the anode plate and deposits on the cathode in the form of a closely adhering layer. By making the proper change in the electrolyte and the anode plate, objects may be plated with gold and other metals.

### QUESTIONS

1. (a) What metals so far studied are found free in nature?  
(b) Considering the metals as a group, which ones would you expect to occur in a free state?
2. How could you prepare the following compounds from metallic copper: cupric nitrate, blue vitriol, cupric hydroxide, cupric sulfide?
3. Describe what takes place when ammonium hydroxide is added drop by drop to a solution of cupric sulfate.

4. (a) What reaction takes place when hydrogen is passed over hot copper oxide? (b) Illustrate the meaning of the following terms by citing the reaction: oxidation, reduction, analysis, synthesis.

5. Mercury dissolves in concentrated nitric acid to form mercuric nitrate. Write the equation for the reaction.

6. (a) How could you distinguish between blue vitriol and cop-peras? (b) corrosive sublimate and calomel? (c) vermillion and Venetian red? (d) lunar caustic and potassium alum? (e) silver and magnesium?

7. How could you prepare the following compounds from silver: silver nitrate, silver sulfide, silver chloride, silver iodide?

8. Suppose you dissolved each of the metals copper and mercury in nitric acid, evaporated the solution to dryness, and ignited the residue. What would be left in each case?

9. Which should be the easier to reduce, the oxide of copper or the oxide of silver?

#### PROBLEMS

1. Which of the ores of copper is richest in copper?

2. (a) What weight of chalcocite would be required to supply copper for 100 kg. of gold coin? (b) 100 kg. of silver coin?

3. What weight of silver nitrate could be prepared from a silver dollar weighing 26.5 g.?

4. What weight of blue vitriol could be prepared from 1 ton of bornite, assuming a yield of 90 per cent of the theoretical?

5. Mercury comes on the market in iron flasks, each flask containing 75 lb. of the metal. The output of mercury in the United States is about 33,000 flasks. Assuming that all of this came from cinnabar, what weight of this mineral must have been required to furnish the above supply?

6. What weight of mercury is required for the preparation of 100 kg. of calomel, assuming that 3 per cent of mercury is lost in the reaction?

7. What weight of silver is required for the preparation of 1000 g. of silver chloride?

8. 1 g. of an ore of silver was dissolved in nitric acid and the silver present precipitated by hydrochloric acid. The resulting silver chloride weighed 0.843 g. Calculate the percentage of silver in the ore.

## CHAPTER XL

### TIN AND LEAD

	SYMBOL	ATOMIC WEIGHT	DENSITY	MELTING POINT	COMMON OXIDES
Tin . . . . .	Sn	118.70	7.30	231.9°	SnO            SnO <sub>2</sub>
Lead . . . . .	Pb	207.20	11.37	327.4°	PbO   Pb <sub>2</sub> O <sub>3</sub> PbO <sub>2</sub>

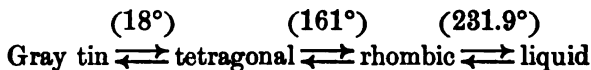
**General.** The elements of smaller atomic weight in Group IV of the periodic classification, including carbon, silicon, titanium, and zirconium, are acid-forming in character and have already been described. The elements of larger atomic weight, of which tin and lead are the well-known representatives, are essentially metals. Germanium is intermediate in character and is so rare as to require little comment, while thorium is a metal and is also very rare. These four elements are not so closely related to each other as are the members of some other groups, and each has its own peculiarities. The more abundant elements, tin and lead, will be described first.

#### TIN

**History and occurrence.** It is difficult to decide just when tin became known to the ancients, but it was undoubtedly at a very early day. In ancient times it was frequently confused with lead, the distinction between the two first clearly appearing in the writings of Pliny, about the beginning of the Christian era. It is found chiefly as the oxide SnO<sub>2</sub>, called *cassiterite*, or *tinestone*, and this is the only commercial ore. Malaya stands first in production, being followed by Bolivia, Banca, and China. Its production in the United States is insignificant.

**Metallurgy.** Since tin occurs as the oxide and is relatively free from other metals, its metallurgy is very simple and consists in reducing the ore with carbon. In some cases the ore is first roasted, to free it from sulfur and arsenic.

**Properties.** Tin occurs in a number of allotropic forms, which pass into each other at definite transition temperatures, the order being as follows:



The first of these transitions is the most interesting, since it takes place at ordinary temperatures. Below  $18^\circ$  ordinary white or tetragonal tin is an unstable form and under some conditions changes into the gray modification, at the same time losing its metallic appearance and crumbling into a powder. The usual form is silver-white, is harder than lead, and is quite malleable. The bending of a bar of tin is accompanied by a creaking noise called *tin cry*. The metal melts at  $231.9^\circ$  and boils at  $2270^\circ$ . Its average density is 7.3.

**Tin plague.** The transformation of white tin into the gray form is sometimes a serious matter. It was first noticed in connection with the deterioration of some organ pipes made of tin, which developed holes and then broke up completely. Later, ingots of tin stored in a Russian customhouse during a very cold winter were found to have crumbled to powder. When the transformation once starts, it continues to spread as long as the temperature is below  $18^\circ$ , and this uncontrollable spread has been called the tin plague, or museum disease, since it sometimes spreads over tin objects in a museum. The speed of the transformation is increased by contact with a solution of certain salts in which tin is slightly soluble.

**Chemical conduct.** At ordinary temperatures tin undergoes practically no change in the air, nor is it attacked by the combined action of air and water; at higher temperatures it is covered with a film of oxide. Dilute acids act upon it very slowly, evolving hydrogen; concentrated hydrochloric acid acting more rapidly, forming the chloride  $\text{SnCl}_2$ . Oxidizing acids, such as nitric acid, convert it into a hydrate of the oxide  $\text{SnO}_2$ .

**Uses of tin.** The great use for tin is in the making of *tin plate*. The process consists in dipping thin sheets of iron into the melted tin and is quite similar to that of galvanizing iron (p. 579). Owing to its resistance to the action of air and weak acids, tin plate is used in many ways, such as in roofing and in the manufacture of tin cans, cooking vessels, and similar articles. Small pipes of block tin are used instead of lead for conveying pure water or liquids containing dilute acids, such as soda water. Many useful alloys contain tin (p. 485). *Pewter* and *soft solder* are alloys of tin and lead.

**Rusting of tin plate.** If the coating of tin on tin plate is scratched through to the iron, the iron will rust faster than if there were no tin covering. The two metals and the water constitute a battery, much like the Daniell cell (p. 648), and in a battery the metal highest in the electrochemical series is the one that is corroded. In the case of galvanized iron the zinc rusts first, and the iron resists rusting as long as any zinc is present.

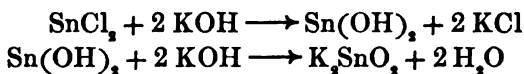
**Soldering and brazing.** The use of solder in joining two metal surfaces depends upon (1) the low melting point of the solder and (2) the fact that it flows over *clean* metal surfaces and sticks to them on cooling. To secure clean surfaces free from oxide a suitable flux must be used which will either *dissolve* the oxide as fast as it forms or will *reduce* it again to metal. The usual fluxes are zinc chloride, ammonium chloride, rosin, and stearin. In *brazing*, or *hard soldering*, the process is essentially the same, except that a low-melting brass is used instead of solder, and borax is used as a flux.

**Compounds of tin.** In its compounds tin is either bivalent or quadrivalent, giving rise to two series of compounds, known as the *stannous* and the *stannic*. In the stannous compounds tin acts for the most part as a base-forming element, its salts resembling those of zinc in a general way.

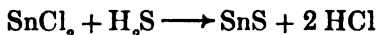
As in the case of zinc, the hydroxide  $\text{Sn}(\text{OH})_2$  is soluble in strong bases, giving a series of compounds known as *stannites*. As a quadrivalent element, tin is chiefly acid-forming, its salts resembling those of silicon. There are also some salts derived from tin as a quadrivalent base, such as the sulfate  $\text{Sn}(\text{SO}_4)_2$ , as well as a great many double and complex compounds.

**Stannous compounds.** Quite a number of stannous salts have been prepared by dissolving either tin or stannous oxide in the appropriate acid. For the most part they are soluble, colorless salts, usually forming a number of hydrates, and are subject to considerable hydrolysis, yielding basic salts. Few of them require special description.

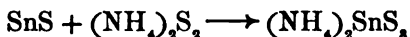
**Stannous oxide (SnO).** This compound is a black powder obtained by warming stannous chloride ( $\text{SnCl}_2$ ) with sodium carbonate and thoroughly washing the product with hot water. The corresponding hydroxide is not known in pure condition, but gives a dehydration product of the composition  $2\text{SnO} \cdot \text{H}_2\text{O}$ , which in turn easily loses its water and is converted into the oxide. The precipitated hydroxide is soluble in alkalies forming *stannites*, as shown in the equations



**Stannous sulfide (SnS).** As prepared by precipitation, stannous sulfide is a dark brown powder obtained by the action of hydrogen sulfide upon a soluble stannous salt:

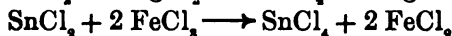
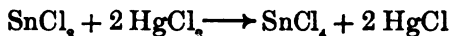


It is insoluble in water, in dilute acids, and in ordinary ammonium sulfide, but is soluble in ammonium polysulfide, forming ammonium sulfostannate:



**Stannous halides.** The four stannous halides are all prepared by the usual methods, stannous chloride ( $\text{SnCl}_2$ ) being the best known. The anhydrous salt is obtained by conducting hydrogen chloride over heated tin. It is a white, crystalline compound, which melts at  $249^\circ$  and boils at  $620^\circ$ . The most familiar hydrate has the composition  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  and is called *tin salt*. It is used in the dyeing industry as a mordant and also as a reducing agent, since it tends to pass very readily to the

quadrivalent condition. This reducing tendency is illustrated in the following equations:



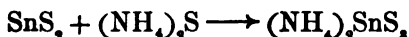
**Stannic compounds.** In its quadrivalent compounds tin usually plays the part of an acid-forming element, the oxide  $\text{SnO}_2$  being essentially an acid anhydride, like silicon dioxide  $\text{SiO}_2$ . Most of these compounds are colorless and are easily hydrolyzed.

**Stannic halides.** With the exception of the fluoride, the stannic halides are easily melted compounds of low boiling point, and have the general physical properties of the halides of acid-forming elements. They are best prepared by acting upon the metal with an excess of the halogen. The chloride will serve as a type of these compounds. This is prepared commercially by treating tin scrap or old tin cans with chlorine, and the product is used for weighting silk. It is a colorless liquid boiling at  $114.1^\circ$  and melting at  $-33^\circ$ . It dissolves in water with strong heat evolution and with considerable contraction in volume. From the solution five different hydrates have been prepared, the most common of which is the pentahydrate  $\text{SnCl}_4 \cdot 5 \text{H}_2\text{O}$ . The chloride also combines directly with many other compounds, such as alcohol and ammonia. Its solution in hydrochloric acid yields chlorostannic acid ( $\text{H}_2\text{SnCl}_6$ ), and the corresponding fluostannic acid ( $\text{H}_2\text{SnF}_6$ ) is also well known. These acids yield a long series of salts, the best known of which is ammonium chlorostannate  $((\text{NH}_4)_2\text{SnCl}_6)$ , called *pink salt*, which finds extensive use as a mordant in the dyeing industry.

In the World War stannic chloride was filled into hand grenades and used to clear dugouts of enemy troops. The explosion of the grenades filled the dugouts with a fine mist of the chloride and in this way vitiated the air so that one could not breathe it without painful suffocation.

**Stannic sulfide ( $\text{SnS}_2$ ).** Stannic sulfide is formed as a bright yellow, amorphous precipitate when hydrogen sulfide is conducted into an acid solution of a stannic compound. It is

insoluble in water and in dilute acids, but is soluble in ammonium sulfide, forming a sulfostannate :



It can be obtained in the form of golden-bronze scales, which feel greasy to the touch, like graphite, by heating a mixture of stannous sulfide, sulfur, and ammonium chloride. This was formerly used as a pigment called *mosaic gold*.

**Stannic oxide ( $\text{SnO}_2$ ).** Stannic oxide is the form in which tin is usually found in nature. As prepared by burning tin in air it is an amorphous powder, called *flowers of tin*. The ignited oxide is not easily attacked by most reagents.

**Hydrates of stannic oxide.** Stannic hydrate ( $\text{Sn}(\text{OH})_4$ ) corresponding to the dioxide is not known in well-defined condition, since it forms a typical colloidal gel resembling  $\text{Si}(\text{OH})_4$ . It is amphoteric in character, but its acid properties predominate. It loses water and passes into a form that is at least approximately represented by the formula  $\text{H}_2\text{SnO}_3$  and is called *stannic acid*. Some salts of this acid have been prepared.

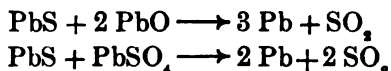
The properties of stannic acid depend very greatly upon the methods employed in its preparation. When precipitated from soluble salts by dilute alkalis it is readily soluble in acids as well as in excess of the alkali. When prepared by the action of nitric acid upon tin it is a curdy, insoluble compound, usually called *metastannic acid*. Forms intermediate between these extremes can be prepared by other methods, and the differences between the several varieties seem to lie in the size of the colloidal particles and in the methods employed in coagulating the colloid, rather than in a different structure of the individual molecules.

## LEAD

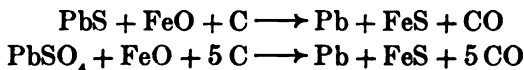
**History and occurrence.** Articles made of lead have been found in Egyptian ruins of great antiquity, and there is no doubt that metallic lead found applications from very early times. The Romans called it *plumbum* and used it for water conduits as we

do today. It does not occur to any appreciable extent in the native state, but is found in combination in many parts of the world. The minerals of most importance to metallurgists are *galena*, or *galenite* ( $\text{PbS}$ ), and to a less extent *cerussite* ( $\text{PbCO}_3$ ) and *anglesite* ( $\text{PbSO}_4$ ). The United States produces over one third of the world's output of lead, the chief producing states being Missouri, Idaho, Utah, and Colorado. The countries which come next to the United States in production are Spain, Mexico, and Germany.

**Metallurgy.** Galenite often contains some silver and gold, and silver ores are often purposely combined with lead ores and the two smelted together. When no silver is present, the ores are roasted in an open oven until they are partially oxidized, and the lead is present as a mixture of sulfide, sulfate, and oxide. Access of air is then cut off and the temperature raised, when the reactions represented in the following equations take place:



Silver-bearing ores are worked in a blast furnace, the bottom of which consists of a large crucible constructed of fire brick. The ore is first roasted and is then charged into the furnace, together with coke and a flux consisting of limestone and iron ore. The chief reactions which produce lead are represented in the equations:



The liquid lead, in which are dissolved the gold and silver, together with varying quantities of copper, antimony, arsenic, and bismuth, collects in the crucible and is tapped off.

**Refining of lead.** The lead obtained in this way is called *hard lead* because of the effect of the alloyed metals. It is softened by the removal of these as follows: The hard lead is melted in a reverberatory furnace with free access of air, until the copper,

arsenic, and antimony are oxidized, together with a considerable quantity of lead. The oxides are skimmed off and the softened lead, which contains the silver, gold, and also bismuth, is run off for desilverizing. Two processes for this purpose are in use in this country.

1. *The Parkes process.* In the Parkes process the lead is run into kettles holding as much as 30 tons, and about 1 per cent of its weight of zinc is added and thoroughly stirred in. These two metals do not mix to any great extent, and gold and silver, as well as copper, are much more soluble in zinc than in lead. Consequently, when the stirring ceases, the zinc, together with most of the precious metals, rises to the top and, when the melt is allowed to cool, hardens to a crust which can be skimmed off. The process is repeated several times. The zinc remaining in the lead is removed by blowing dry steam and air through the liquid lead, which oxidizes the zinc; or it is oxidized as in the original softening. The zinc crusts are distilled from a retort, by which process the zinc is recovered, to be used again, and the residue is cupelled as with silver to give *doré* bars.

2. *The Betts process.* In the Betts process the lead is refined by electrolysis, as in the case of copper. A sheet of pure lead serves as cathode, a thick plate of crude lead as anode, and a solution of lead fluosilicate ( $\text{PbSiF}_6$ ), together with some colloidal material, such as gelatin, as electrolyte. The lead deposits upon the cathode, the iron remains dissolved in the electrolyte, and the copper, bismuth, antimony, arsenic, silver, and gold are left undissolved as a skeleton of the anode. A considerable quantity of bismuth is recovered from this source.

**Properties of lead.** Pure lead is a silvery metal of density 11.37, which melts at  $327.4^\circ$  and boils at  $1525^\circ$ . It is dimorphous, crystallizing either in the isometric or in the monoclinic system. It is the softest of all the heavy metals and is a moderately good conductor of electricity. It is quite malleable, but has little strength.

**Chemical conduct.** Lead is a moderately active metal, standing next above hydrogen in the electrochemical series. Its true activity is often concealed by the fact that so many of its compounds are insoluble and form protective coatings upon its surface. It quickly tarnishes in air, owing to the formation of a bluish-gray oxide ( $\text{Pb}_3\text{O}_2$ ). It is acted upon with vigor by fluorine, and with less intensity by the other halogens. With the exception of

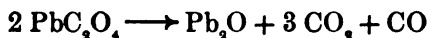
hydrochloric and sulfuric acids, which form insoluble compounds with lead, most acids (even very weak ones) act upon it, forming soluble lead salts. Hot concentrated hydrochloric and sulfuric acids also attack it slightly.

**Uses of lead.** The industrial uses of lead are very numerous. Chief among them are the manufacture of water pipes, of storage batteries, and of structures to be exposed to acids, such as the lead chambers in a sulfuric acid plant. A great many alloys contain lead, among them being type metal, antifriction metals of various kinds, shot, pewter, and solder (p. 485). About one third of the yearly output is used in the manufacture of paints and is permanently lost.

**Compounds of lead.** With very few exceptions lead is either bivalent or quadrivalent in its compounds. The bivalent hydroxide  $\text{Pb}(\text{OH})_2$  is essentially a base and gives rise to a series of well-defined salts, most of which are colorless, since lead gives them no characteristic color. They are somewhat hydrolyzed in solution and yield numerous basic salts. The quadrivalent hydroxide  $\text{Pb}(\text{OH})_4$  is an acid, and but few of its derivatives are well defined. All compounds of lead which are at all soluble are poisonous, and lead workers of all classes are subject to the occupational disease known as *lead colic*.

**Oxides of lead.** Lead forms five oxides, of which three are simple oxides having the formulas  $\text{Pb}_2\text{O}$ ,  $\text{PbO}$ , and  $\text{PbO}_2$ . The other two, whose formulas are  $\text{Pb}_3\text{O}_4$  and  $\text{Pb}_8\text{O}_7$ , are complex compounds.

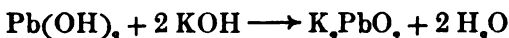
**Lead suboxide ( $\text{Pb}_3\text{O}$ ).** This compound is obtained as a grayish-black powder by carefully heating lead oxalate:



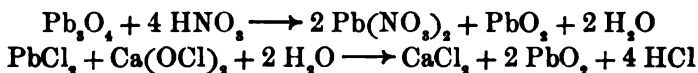
It forms as a thin film on the surface of exposed lead, to which it gives the characteristic lead color.

**Lead monoxide (litharge) ( $\text{PbO}$ ).** This oxide appears to exist in a number of modifications, the colors of which range from yellow and light brown to red, and the color of the commercial product varies considerably in consequence. It is a highly

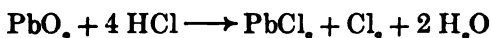
crystalline compound, but commercial litharge, obtained as a by-product in a number of processes, is usually a fine powder. The corresponding hydroxide  $\text{Pb}(\text{OH})_2$  is a white solid obtained by precipitation and is very slightly soluble in water. It is soluble in acids, giving the best-known salts of lead, and in the strong alkalies, forming compounds called *plumbites*:



**Lead dioxide ( $\text{PbO}_2$ ).** This compound is formed by the action of nitric acid on red lead ( $\text{Pb}_3\text{O}_4$ ) as well as by the action of calcium hypochlorite on a lead salt:



It is also obtained as a coating upon the anode when solutions of lead salts are subjected to electrolysis. It is a chocolate-brown powder and is a good oxidizing agent. Thus, with hydrochloric acid it acts like manganese dioxide, liberating chlorine:



It is important in the construction of storage cells (p. 677).

**Lead nitrate ( $\text{Pb}(\text{NO}_3)_2$ ).** This salt is readily obtained by dissolving metallic lead or litharge in nitric acid. It crystallizes in octahedra and is easily soluble in water.

**Lead acetate ( $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ ).** The acetate is obtained by dissolving litharge in concentrated acetic acid, from which it crystallizes in snow-white, monoclinic crystals of the composition  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3 \text{H}_2\text{O}$ . It is known as *sugar of lead* because of its sweetish taste. Two soluble basic acetates are known, the more familiar one having the composition expressed by the formula  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)\text{OH} \cdot \text{H}_2\text{O}$ . The nitrate and acetate are the important soluble salts of lead.

**Lead sulfide ( $\text{PbS}$ ).** Native lead sulfide (*galena*) has almost the appearance of lead itself, save that it is conspicuously crystalline. Prepared by precipitation, it is a black, amorphous solid, insoluble in water and in acids.

**The halides of lead.** Lead chloride ( $\text{PbCl}_2$ ) is precipitated as a white, crystalline powder when a soluble lead salt is treated with a soluble chloride. It is very sparingly soluble in cold water and in acids, but is more soluble in hot water. The bromide  $\text{PbBr}_2$  and the iodide  $\text{PbI}_2$  resemble the chloride in properties, save that the iodide is golden yellow in color. A tetrachloride ( $\text{PbCl}_4$ ) corresponding to the dioxide has been prepared.

**Lead carbonate ( $\text{PbCO}_3$ ).** Normal lead carbonate, which occurs in nature as *cerussite*, may be prepared as a white, crystalline powder by precipitating a solution of a lead salt with a solution of sodium carbonate. Several basic carbonates of lead are known, but the one having the formula  $2\text{Pb}(\text{CO}_3)_2 \cdot \text{Pb}(\text{OH})_2$ , called *white lead*, is of much technical importance, since it is the basis of most paints.

**Manufacture of white lead.** White lead can be prepared by a number of processes, but none of them seems to produce a product of as desirable physical properties as the old Dutch process, which has been used for centuries, though with many improvements. In this process the lead is cast into perforated plates, which are placed loosely upon each other in a crock of the shape shown in Fig. 176, the ledge formed by the constriction in the crock supporting the plates. Under them is poured a suitable quantity of dilute acetic acid, and the crocks so charged are placed in banks and covered with stable manure or spent tanbark. The heat of fermentation in the latter warms the acid, the fumes of which attack the lead, forming acetate. The carbon dioxide from the fermentation enters into reaction with the acetate and produces the basic carbonate, regenerating acetic acid, which acts again upon the lead. The process continues until the plates are almost completely converted into the desired compound.

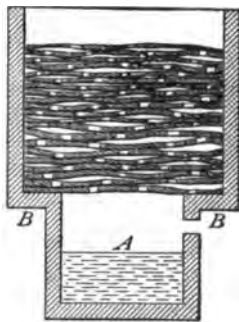


FIG. 176

**Paints.** The manufacture of paints is a very extensive chemical industry, and absorbs a large percentage of all the lead produced. A paint consists of three essential ingredients:

1. **The vehicle, or liquid medium.** This must be an oil which will dry rapidly and harden in drying to a more or less flexible, hornlike body. These changes in the oil are due to oxidation by the air. A number of different

oils will serve this purpose, but linseed oil has long been used as the standard drying oil. It is customary to add to it a *dryer*, made by boiling some of the oil with oxides of manganese, lead, or cobalt. The oxides enter into combination with the oil and assist catalytically in its oxidation.

2. *The body.* The body of the paint must be some solid material, suspended in the oil, which will give a smooth and waxy surface as the paint dries, and will have good covering power. While white lead meets these requirements, it is moderately expensive and it also blackens when exposed to hydrogen sulfide, which is likely to be present in the air in cities. Other bodies are now frequently combined with the lead or replace it altogether, among them being zinc oxide, China clay (or kaolin), barium sulfate, and a product called *lithopone*. This is a combination of zinc sulfide and barium sulfate produced by precipitating barium sulfide with zinc sulfate:

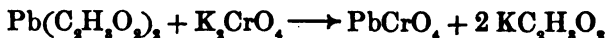


For some purposes these materials are a real advantage, and they are not to be regarded as adulterants unless sold as white lead.

3. *The pigment, or coloring matter.* In the case of white paints the body serves also as the coloring matter. For other colors a specific pigment must be added. In most cases these are metallic oxides or salts, and are frequently natural products. Sometimes they are prepared by precipitating an amorphous body (usually a colloid) in the presence of an organic dye, the dye being adsorbed by the precipitate and giving it a color. Such pigments can be prepared in endless variety of color and are called *lakes*. Usually they are not as permanent as a mineral pigment.

**Lead sulfate ( $\text{PbSO}_4$ ).** Lead sulfate is a white, crystalline solid, insoluble in water and dilute acids. It is therefore formed as a precipitate whenever the ions  $\text{Pb}^{++}$  and  $\text{SO}_4^{--}$  are brought together in solution. The sulfate is soluble in concentrated sulfuric acid, but precipitates again when this is diluted.

**Lead chromate ( $\text{PbCrO}_4$ ).** This bright yellow salt, called *chrome yellow*, results as a precipitate when a soluble lead salt is treated with a soluble chromate:

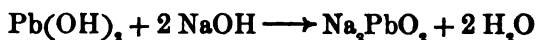


By boiling the normal chromate with a solution of an alkali, a brick-red basic salt is obtained, called *chrome red*, which has the formula  $\text{PbCrO}_4 \cdot \text{PbO}$ . Both of these chromates are used as paint pigments.

**Lead arsenate ( $\text{Pb}_3(\text{AsO}_4)_2$ ).** This compound is a white, insoluble powder difficultly soluble in water, prepared by treating lead acetate with sodium arsenate. It is quite extensively employed as an insecticide (p. 477).

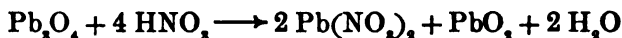
**Acids of lead.** Both of the hydroxides of lead have feeble acid properties, dissolving in solutions of the alkalis to form salts.

**The plumbites.** The salts derived from plumbous hydroxide acting as an acid are called *plumbites*. The formation of sodium plumbite is represented in the equation



**The plumbates.** The derivatives of plumbic hydroxide, acting as an acid, are called *plumbates*. Some of these are *orthoplumbates*, derived from orthoplumbic acid ( $\text{H}_3\text{PbO}_4$ ), while others are *metaplumbates*, derived from metaplumbic acid ( $\text{H}_2\text{PbO}_4$ ). The oxide  $\text{Pb}_2\text{O}_3$  is really lead metaplumbate ( $\text{PbPbO}_3$ ).

**Lead orthoplumbate (minium, red lead) ( $\text{Pb}_3\text{O}_4$ ).** The formula  $\text{Pb}_3\text{O}_4$  is usually assigned to this salt, though its composition is more satisfactorily expressed by the formula  $\text{Pb}_2\text{PbO}_4$ . It is a bright red powder obtained by heating litharge in the air to about  $450^\circ$ , and is valuable as a paint pigment. When treated with nitric acid, two thirds of the lead passes into solution, the other third remaining as the insoluble dioxide:



**Storage cell.** The storage cell, or *accumulator*, plays an important part in modern electrical developments. Its fundamental characteristic is that the chemical action upon which it depends is reversible. The chemical action taking place when the cell is delivering current is reversed when a current is conducted through the cell in an opposite direction. Electrical energy can therefore be stored in the cell as chemical energy and drawn off again, when desired, as electrical energy. Many chemical reactions are adapted to this purpose, including those which take place in the common Daniell cell (p. 648), but there are a great many purely physical and mechanical requirements which are difficult to meet, and in practice only two types of cells have proved successful. These are usually known as the chloride accumulator and the Edison cell.

In the accumulator (Fig. 177) the electrodes are made of a skeleton of lead. When ready for use, the one plate is covered with a thick deposit of spongy lead, which is the active material; the other is similarly covered

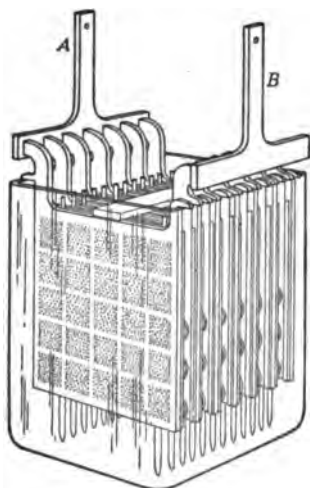


Fig. 177

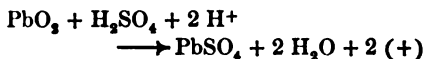
with a layer of lead dioxide. The electrolyte is moderately dilute sulfuric acid. A number of pairs of such plates are arranged together in one cell. When these pairs are connected by a wire, the reactions are as follows:

At the lead plate:



The insoluble lead sulfate deposits in the spongy lead, and the negative charge (2 electrons) is given up to the plate.

At the lead dioxide plate:



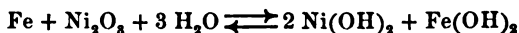
The lead sulfate deposits with the dioxide, and the positive charge is given up to the plate (2 electrons withdrawn from

it). The electrons flow through the external circuit from the lead plate to the dioxide plate. The complete equation is therefore



It will be seen that the action of the cell results in bringing the two plates to an identical condition and in withdrawing sulfuric acid from the electrolyte. The cell is never allowed to come entirely to this discharged condition. When the current is reversed, the two plates are restored to their original state.

In the Edison cell the one plate is of iron, the other is covered with a deposit of the higher oxide of nickel ( $\text{Ni}_2\text{O}_3$ ), and the electrolyte is a solution of potassium hydroxide. The reactions are not so well understood as in the case of the lead battery, but in a general way the following equation represents the reversible reaction:



**Germanium.** Germanium was discovered in 1866 by Winkler, in connection with some analyses of the rare mineral *argyrodite*. His analyses failed to account for from 6 to 7 per cent of the mineral, and a long and careful search resulted in the discovery of the new element. It was found to fulfill in a remarkable way the predictions of Mendeléeff for the

properties of an undiscovered element which should follow silicon in the fourth group, and which he provisionally named *ekasilicon*.

In the elementary condition, germanium is a soft, crystalline, metallic substance having a density of 5.47 and melting at  $958^{\circ}$ . It forms two oxides of the formulas  $\text{GeO}$  and  $\text{GeO}_2$ , each of which gives rise to a series of compounds. Those in which germanium is quadrivalent recall the corresponding compounds of carbon and silicon. Those derived from the lower oxide have been very little investigated.

**Thorium.** Thorium, named in honor of the Scandinavian god Thor, was discovered by Berzelius in 1828. The element is an essential constituent of a few rare minerals, notably *thorite* ( $\text{ThSiO}_4$ ), but for the most part it is found in very small concentrations in various minerals, especially in those which are rich in the rare earths (p. 599). Commercially its compounds are almost entirely obtained from *monazite sand*.

This is commonly found as a constituent of beach sands and consists of cerium phosphate, associated with the phosphates of other rare earths. This sand derives its main importance from the fact that it contains thorium oxide varying in amounts from traces up to 25 per cent, and serves as the source of all the thorium used in the manufacture of gas mantles (p. 422). It is found in North Carolina and South Carolina, and considerable material has been obtained from this source. At present, practically all our supply comes from Brazil and southern India.

The metal is very difficult to prepare in pure condition, and is best obtained by reducing the oxide with *mixed metal* (p. 601). It is a heavy metal somewhat resembling platinum in luster, hardness, and ductility. Its melting point is considerably above that of iron. In its compounds thorium always acts as a quadrivalent metal, and it forms a long series of simple salts, as well as many double ones. The chief salt of commerce is the nitrate, the usual hydrate of which has the formula  $\text{Th}(\text{NO}_3)_4 \cdot 12 \text{H}_2\text{O}$ . This salt finds an extensive use in the manufacture of gas mantles of the Welsbach type.

**Radioactivity of thorium.** The atomic weight of thorium is 232.15 and this is the largest possessed by any of the elements,

excepting uranium (238.2). It is therefore extremely interesting to find that compounds of thorium, like those of uranium, possess a peculiar property known as radioactivity. As this property was discovered in connection with the latter element, in which it is much more pronounced, a discussion of it will be delayed until the compounds of uranium are described (p. 702).

### QUESTIONS

1. Contrast the action of hydrochloric acid on tin, mercury, zinc, and aluminium.
2. Name the important alloys of tin.
3. (a) How could you distinguish between lead and tin? (b) tin and silver?
4. Contrast the action of hydrochloric acid upon  $\text{PbO}_2$ ,  $\text{MnO}_2$ , and  $\text{BaO}_2$ .
5. How could you distinguish between red lead, cinnabar, Venetian red, and vermilion?
6. Point out any similarity in properties between lead and tin.
7. (a) Mention the metals that form insoluble sulfates; (b) insoluble chlorides; (c) insoluble nitrates.
8. White lead used in paint sometimes contains barite. How could you detect its presence?
9. Which pigment would you prefer for painting the interior of a chemical laboratory, white lead, zinc oxide, or lithopone?

### PROBLEMS

1. What weight of cassiterite would be required to make 100 kg. of Babbitt metal (p. 485)?
2. Assuming a yield of 95 per cent of the theoretical, what weight of chrome yellow was obtained when 100 g. of lead was converted into sugar of lead, and this into chrome yellow?
3. What weight of white lead will 1 ton of lead give?
4. When treated with acids, what volume of carbon dioxide at  $20^\circ$  and 740 mm. will 100 g. of a sample of pure white lead yield?
5. (a) What is the percentage of tin in cassiterite? (b) of lead in galena?

## CHAPTER XLI

### MANGANESE AND CHROMIUM

NAME	SYMBOL	ATOMIC WEIGHT	DENSITY	MELTING POINT	FORMULAS OF ACIDS
Manganese	Mn	54.93	8.01	1230°	$H_2MnO_4$ and $HMnO_4$
Chromium	Cr	52.00	7.30	1615°	$H_2CrO_4$ and $H_2Cr_2O_7$

**General.** The elements manganese and chromium occur in different periodic families, but there are certain advantages in considering them together. Neither one is very closely related to any other well-known element, manganese having no companion element in the seventh group and chromium differing considerably from the other members of its family. On the other hand, the two elements have a good many characteristics in common.

In their chemical conduct manganese and chromium present about the greatest variety of all the elements, with the exception of carbon. In describing the compounds of these elements it will be possible to mention only those which will serve to illustrate the characteristics of each series.

### MANGANESE

**History and occurrence.** While manganese is not at all a rare element, its ores were confused with those of iron by the earlier chemists, and it was not until the time of Scheele (1774) that the mineral pyrolusite was shown to be essentially different from magnetite and to contain a different metal. Manganese occurs in nature chiefly as the dioxide  $MnO_2$ , known as *pyrolusite*. The largest deposits are in Brazil and India. During the

World War, when it was difficult to secure adequate supplies from Brazil, considerable manganese ore was mined in the United States; under ordinary conditions, however, the production is very limited. The element also occurs in the form of a number of other oxides and their hydrates, and is very widely distributed in small percentages through many minerals and soils. To some extent it is absorbed by plants.

**Metallurgy.** Entirely pure manganese is difficult to prepare, since the metal tends to combine with many of the usual reducing agents, such as carbon. It is most easily prepared in a fairly pure state by the reduction of its oxide by aluminium (Goldschmidt method) or by carefully controlled reduction by carbon in an electric furnace. It is much more frequently produced as an alloy by the simultaneous reduction of oxides of iron and manganese. The alloys produced in this way containing up to about 20 per cent of manganese are known as *spiegel iron*, while those containing higher percentages are termed *ferromanganese*. The ordinary ferromanganese contains about 80 per cent manganese, and from 4 to 6 per cent of carbon.

**Properties and conduct.** Manganese is a hard and brittle metal somewhat resembling iron in appearance, but often with a slightly reddish tint. It melts at about  $1230^{\circ}$  and boils at about  $1900^{\circ}$ , both these temperatures being considerably lower than the corresponding ones for iron. Its density is 8.01.

In chemical conduct manganese most closely resembles iron. It oxidizes in the air with great ease when pure, but less rapidly when it contains some carbon. It liberates hydrogen from dilute acids and from water.

**Uses.** The great use of manganese is in connection with the steel industry. It is usually added to the molten steel, in the form of ferromanganese. This serves not only to introduce the proper amount of manganese into the steel, but it also acts as a deoxidizer and as a medium for introducing the desired amount of carbon. *Manganese bronze* contains principally copper and manganese and resists corrosion. *Manganin* consists of

copper, nickel, and manganese and is used as standard resistance wire in electrical measurements.

**Compounds of manganese.** Manganese yields compounds corresponding to five different valences. The element differs from nearly all the elements we have so far studied in that in its *lower* valences it plays the part of a *positive metallic ion*, yielding salts such as  $\text{MnCl}_2$  and  $\text{MnCl}_3$ , corresponding to the salts of iron; while in its *higher* valences it is a *constituent of the negative ion of an acid*, the best known of which have the formulas  $\text{H}_2\text{MnO}_4$  and  $\text{HMnO}_4$ . Elements of this kind are called *metallo-acid* elements, and nearly all the elements that remain to be considered are of this type.

The changes that accompany the oxidation and reduction of compounds of manganese are therefore much more complicated than those that occur in the oxidation of a ferrous to a ferric salt, or the reduction of a ferric to a ferrous salt; for in both ferrous and ferric salts the iron plays the part of a metallic ion, while in the case of manganese a salt of the type  $\text{MnCl}_2$  is changed by oxidation into an acid of the formula  $\text{H}_2\text{MnO}_4$  or  $\text{HMnO}_4$ .

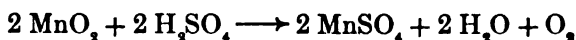
These rather perplexing changes will be understood most clearly if we start with the compound  $\text{MnO}_2$ , and study the effect of reagents upon it.

**Manganese dioxide ( $\text{MnO}_2$ ); the manganites.** Manganese dioxide occurs in nature not only in the form of the hard, dense mineral *pyrolusite* ( $\text{MnO}_2$ ) but in a number of hydrated forms and in combination with other oxides, as in *hausmannite* ( $\text{MnO}_2 \cdot 2\text{MnO}$ ). Owing to the fact that pyrolusite readily gives up oxygen, which is not a very common property in minerals, it has long been used as an oxidizing agent in the industries, especially in the production of chlorine. It is also used in glass making (p. 605). As prepared in the laboratory, it is a dark brown to black powder. It is produced upon the anode when manganese salts are subjected to electrolysis, like the corresponding dioxide of lead.

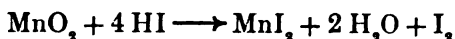
Like the latter compound, it acts as the anhydride of a weak acid, and salts corresponding to the plumbates and stannates may be obtained by heating the dioxide with the oxides of basic elements, such as calcium. These salts are called *manganites*, the formula of the calcium salt being  $\text{CaMnO}_3$ , or  $\text{CaO} \cdot \text{MnO}_2$ . The corresponding manganous salt is  $\text{MnO} \cdot \text{MnO}_2$ , or  $\text{Mn}_2\text{O}_3$ , which occurs in nature as *braunite*. Manganese dioxide also has very feeble basic properties yielding the chloride  $\text{MnCl}_2$ . In the manganites and in manganese dioxide the valence of manganese is 4.

**Effect of reducing agents upon manganese dioxide.** When manganese dioxide is treated with a *reducing* agent, the manganese tends to drop from a valence of 4 to a valence of 2 (or to a valence of 3, if the reducing agent is a very weak one). In these valences it plays the part of a bivalent or a trivalent metal just like iron, forming salts in which the manganese is the positive ion. Consequently *the reduction takes place most readily in acid solution*, which supplies the necessary anions.

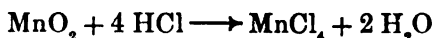
Thus, when heated with sulfuric acid the dioxide yields manganous sulfate, and free oxygen is evolved:



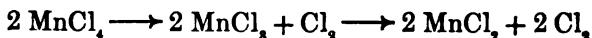
With the strong reducing agent HI, also an acid, the reaction is



With the very weak acid reducing agent HCl, the first reaction appears to be ordinary double decomposition:



But the tendency of manganese to go down to a valence of 2 is so strong that the tetrachloride decomposes by steps:

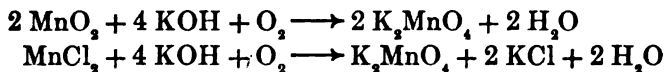


It is possible therefore to make the following general statement: *Under reducing conditions, and in the presence of an acid, all manganese compounds tend to form manganous (bivalent) salts.*

**Manganous salts.** The manganous salts are quite stable, well-crystallized compounds. The soluble ones are light pink in color, while those prepared by precipitation, such as the sulfide ( $\text{MnS}$ ) and the carbonate ( $\text{MnCO}_3$ ), are nearly white. All these salts tend to form many hydrates, the one obtained in any given case, depending upon the temperature at which the salt crystallizes. The most familiar hydrate of the chloride has the composition  $\text{MnCl}_2 \cdot 4 \text{H}_2\text{O}$ , and the sulfate obtained by crystallization at room temperature is  $\text{MnSO}_4 \cdot 4 \text{H}_2\text{O}$ , though at somewhat lower temperatures the hydrate with five, as well as with seven, molecules of water can be obtained. The corresponding hydroxide  $\text{Mn}(\text{OH})_2$  is obtained as a white precipitate by treating a solution of any manganous salt with a soluble base. Under these conditions, however, it is in contact with a *base*, and it oxidizes in the air with great rapidity, changing into hydrates of higher oxides.

**Manganic salts.** While a number of manganic salts have been described, few of them are well defined. There is evidence of the existence of a chloride ( $\text{MnCl}_3$ ) and a sulfate ( $\text{Mn}_2(\text{SO}_4)_3$ ), as well as of a few other trivalent salts. Most of these salts have a deep cherry-red color. None of them play an important part in the chemistry of manganese.

**Effect of oxidizing agents upon manganese dioxide.** When manganese dioxide is treated with a strong *oxidizing agent*, the manganese tends to increase in valence to either 6 or 7. The compounds so formed are *acids* in character, the manganese being a constituent of the anion as indicated in the formulas  $\text{H}_2\text{MnO}_4$  and  $\text{HMnO}_4$ . Since the products of the oxidation are acids, the oxidation is greatly helped along by keeping an excess of alkali present to neutralize the acids. With a large excess of alkali, a manganate is formed according to the equations



*Under oxidizing conditions, and in the presence of a base, all manganese compounds tend to give a manganate in which manganese has a valence of 6.*

**The manganates; manganic acid ( $\text{H}_2\text{MnO}_4$ ).** In accordance with the principles and equations just explained, the manganates of the alkali metals are obtained by fusing manganese dioxide with an alkali in free access of air to supply oxygen. The dark green mass so obtained is soluble in water, and from the solution green crystals of the alkali salts  $\text{K}_2\text{MnO}_4$  and  $\text{Na}_2\text{MnO}_4$  have been isolated. These salts, like the free manganic acid ( $\text{H}_2\text{MnO}_4$ ), are very unstable and are never prepared in pure form for commercial purposes. The salts are isomorphous with the corresponding sulfates which they resemble in formulas.

**Potassium permanganate ( $\text{KMnO}_4$ ).** When potassium manganate ( $\text{K}_2\text{MnO}_4$ ) is dissolved in water it undergoes extensive hydrolysis, and the valence of the manganese again changes. The reaction is a very interesting one for it is *reversible*, and is at the same time a good example of *self-oxidation*. It is as follows:



By neutralizing the KOH formed in the reaction (by means of  $\text{CO}_2$  or  $\text{HNO}_3$ ) the reaction becomes a completed one, the main product being *potassium permanganate*,  $\text{KMnO}_4$ . By evaporation of the solution the salt crystallizes in deep purple crystals.

From the equation it will be seen that one third of the manganese is lost in making the permanganate in the way described. The salt may be prepared by the electrolysis of solutions of the manganate, utilizing the powerful oxidizing action of the oxygen evolved at the anode to effect the oxidation of the manganate.

Potassium permanganate is a powerful oxidizing agent and is an indispensable reagent in chemical analysis. It is also extensively used as a disinfectant. For the latter purpose it is not necessary to use the pure salt, and a solution of sodium and potassium permanganate is sold for disinfecting purposes under the name of Condry's Fluid.

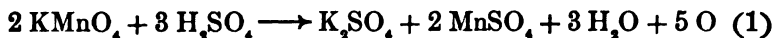
**Other permanganates.** All of the permanganates are very soluble salts, silver permanganate being the least soluble. In general they are prepared from free permanganic acid ( $\text{HMnO}_4$ ), which is in turn obtained by the electrolysis of solutions of potassium permanganate. All of the permanganates,

as well as the free acid, give solutions of the same intense purple-red color. As a rule they are isomorphous with the corresponding perchlorates.

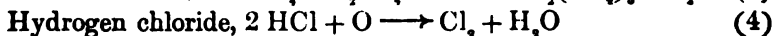
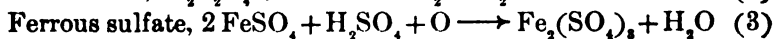
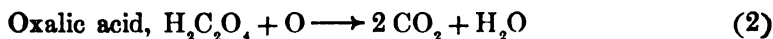
Sodium permanganate ( $\text{NaMnO}_4 \cdot 3 \text{H}_2\text{O}$ ) is an extremely soluble salt and on this account is difficult to prepare in the form of pure crystals. However, some of the difficulties attending its preparation have been overcome so that the solid sodium salt is now on the market. Solutions of sodium permanganate are sold as disinfectants.

**Oxidizing action of potassium permanganate.** Potassium permanganate finds extensive use as an oxidizing agent, both in the industries and in the laboratory. Its oxidizing action is easily understood when it is remembered that manganese can play the part either of an acid-forming element of high valence (7) or of a base-forming element of lower valence (2 or 4). The decomposition of the permanganate may take place in two different ways, depending upon whether the reaction occurs in an acid solution or in one that is neutral or basic.

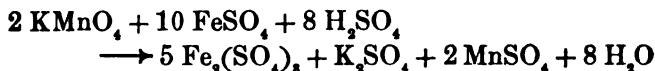
1. *Oxidation in acid solution.* When the permanganate is brought into a solution of an acid, *both the potassium and the manganese tend to form salts with the given acid* while the oxygen of the permanganate unites with the hydrogen of the added acid to form water. This brings about a complete rearrangement of the constituents of the permanganate with the liberation of oxygen:



This action is not very noticeable unless some reducing agent is present to take up the oxygen, under which conditions it is very rapid, even at ordinary temperatures. Since the permanganate solution is intensely colored, while the products of oxidation are, as a rule, almost colorless, the completion of the oxidation can be determined with great accuracy. This combination of properties makes potassium permanganate of the greatest service in chemical analysis. The following equations illustrate the oxidizing power of the permanganate:



The complete equation can be obtained by combining these with equation (1) above. With ferrous sulfate it is as follows:

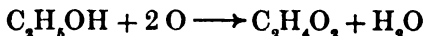


It will be recalled that the reactions represented in equations (1) and (4) serve as a common laboratory method for preparing chlorine (p. 193).

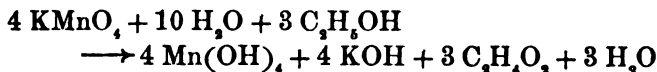
**2. Oxidation in neutral or basic solution.** In neutral or basic solution the tendency is for the manganese to become quadri-valent, forming the compound  $\text{Mn}(\text{OH})_4$ . The reaction, which takes place with noticeable rapidity only in the presence of a reducing agent, is expressed in the following equation:



In very dilute alkaline solution, alcohol is oxidized to acetic acid:



The combined equation is as follows:



## CHROMIUM

Chromium was discovered by the French chemist Vauquelin in 1797, during an investigation of the rather rare mineral *crocoite* ( $\text{PbCrO}_4$ ). Its chief occurrence in nature is in the form of *chromite*, or *chrome iron ore* ( $\text{Fe}(\text{CrO}_2)_2$ ), but in traces it is rather widely distributed in minerals, many of which, such as the emerald, appear to owe their green color to its compounds. The commercial supply of chrome ore comes from Rhodesia, New Caledonia, and Greece, with smaller quantities from California.

**Preparation and properties.** The pure metal is best prepared by the Goldschmidt process, and a somewhat less pure product by careful reduction of the oxide by carbon in an electric furnace, any excess of carbon being avoided. It is a highly crystalline,

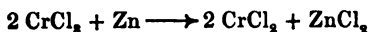
brilliant, silvery metal, very hard and brittle. Specimens containing a little carbon are very much harder than the pure metal. Its density is 7.3, its melting point 1615°, and its boiling point about 2200°.

The element is unoxidized in air at all ordinary temperatures, but when it is finely powdered and sufficiently heated, it burns with great brilliancy. It displaces hydrogen from dilute acids, forming chromous salts, but it is not attacked by oxidizing acids like nitric acid, assuming instead a passive condition (p. 621).

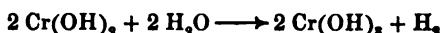
**Uses.** The metal is quite extensively used in the steel industry, since its alloys with iron are very hard and well adapted to special uses such as the manufacture of high-speed lathe tools (p. 621). For such purposes the metal is prepared in the form of *ferrochromium* by the reduction of chrome iron ore with carbon, the product containing from 60 to 70 per cent of chromium and from 1 to 8 per cent of carbon. Its alloys with nickel, cobalt, and copper are also very hard and strong, the one consisting of chromium, tungsten, and cobalt, and known as *stellite*, being especially well adapted to the manufacture of cutlery.

**Compounds of chromium.** Like manganese, chromium can exist in a number of stages of oxidation, its chief compounds being derived from oxides of the formulas  $\text{CrO}$ ,  $\text{Cr}_2\text{O}_3$ , and  $\text{CrO}_3$ . The first of these is always basic; the second, like the corresponding oxide of aluminium, is predominantly basic, but to a limited extent plays the part of an acid anhydride; the third is always acid in character. Nearly all the compounds of chromium are highly colored in shades of blue, green, violet, red, and yellow — a fact which originally suggested the name of the element, from the Greek word meaning "color."

**Chromous compounds.** Chromous salts, corresponding to the oxide  $\text{CrO}$ , are most easily prepared by dissolving chromium in the appropriate acid, the hydrogen evolved in the reaction preventing the salt from oxidizing. Solutions containing them can also be prepared by the reduction of chromic salts by means of such metals as zinc:



If sodium acetate is added to the solution so obtained, the difficultly soluble chromous acetate  $(\text{Cr}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{H}_2\text{O})$  is obtained in the form of deep red crystals, and this is the best-known chromous salt in the solid state. The corresponding hydroxide  $\text{Cr}(\text{OH})_2$  is obtained as a yellow precipitate, which oxidizes with such ease that it slowly decomposes water, with evolution of hydrogen:

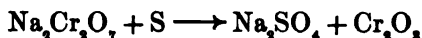


Chromous salts act in the same general way:



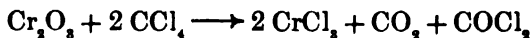
**Chromic compounds.** The compounds derived from chromic oxide ( $\text{Cr}_2\text{O}_3$ ) are the stable compounds of chromium as a base-forming element. They are analogous to the corresponding salts of aluminium and ferric iron, and, like these, are quite extensively hydrolyzed in solution. Chromic salts of most of the familiar acids are known.

**Chromic oxide ( $\text{Cr}_2\text{O}_3$ ).** This oxide can be obtained by the various methods available in the preparation of oxides; it is a green powder, the exact shade of which depends upon its physical condition. In the crystalline state it is very bright green in color, but otherwise it bears a strong resemblance to corundum. For use as a pigment it is usually prepared by heating sodium dichromate with a suitable reducing agent, sulfur serving very well:



The hydroxide ( $\text{Cr}(\text{OH})_3$ ), as prepared by precipitation, is a rather dark green, amorphous solid, which gives a number of dehydration products of indefinite formulas.

**Chromic chloride ( $\text{CrCl}_3$ ).** This compound will serve very well to illustrate some of the peculiarities of chromic salts in general. It can be obtained in the form of beautiful violet-colored, pearly scales by preparing it in the absence of water, as by heating chromic oxide in the vapors of carbon tetrachloride:



It is apparently insoluble in water, but it dissolves upon long standing (or, much more rapidly, through the catalytic action of a trace of a chromous compound), forming a green solution. Under

favorable conditions green crystals deposit from this solution, having the composition expressed in the formula  $\text{CrCl}_3 \cdot 6 \text{H}_2\text{O}$ . If silver nitrate is added to this solution, only two thirds of the chlorine is precipitated, which indicates that one of the chlorine atoms is in a different condition from the other two and is not an ion. Upon long standing the solution turns violet in color and deposits crystals of a gray-blue tint. These also have the formula  $\text{CrCl}_3 \cdot 6 \text{H}_2\text{O}$ , and their solution acts normally with silver nitrate."

Many other chromic salts exist in two modifications analogous to these two soluble salts. Long standing and low temperature favor the formation of the violet form, while rapid formation and hot solutions produce the green variety. In many instances there is doubtless hydrolysis, which results in the formation of green basic salts; but that there are complexes of other kinds is shown by the fact that the green modifications rarely act normally with precipitating reagents.

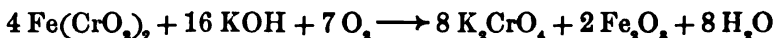
**Other chromic salts.** Of the other chromic salts the sulfate  $\text{Cr}_2(\text{SO}_4)_3$  is the best known. The violet form has the composition  $\text{Cr}_2(\text{SO}_4)_3 \cdot 15 \text{H}_2\text{O}$ . A number of green modifications with varying compositions are known. When crystallized along with potassium or ammonium sulfate, chromic sulfate forms an alum, which yields large, ruby-colored octahedra of great perfection of form. *Potassium chrome alum* ( $\text{KCr}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$ ) has extensive use in the leather industry. In solution it yields *chromic hydroxide* by hydrolysis, and this compound acts upon animal skins in much the same way as tanbark does, but very much more rapidly.

Like aluminium and ferric iron, trivalent chromium forms no carbonate, nor does it form a sulfide by precipitation methods. Reactions which would normally lead to the formation of these compounds produce the hydroxide instead, as is true with most of the trivalent metals.

**Chromites.** Chromic hydroxide, like aluminium hydroxide, is soluble in excess of the alkalis. This does not seem to be due to the formation of a soluble chromite corresponding to an aluminate (p. 591) but to a colloidal dispersion of the hydroxide by the alkali. When the solution is

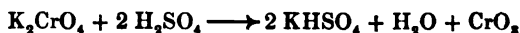
boiled the hydroxide is again precipitated. By fusion methods *chromites* may be obtained, derived from the partial anhydride  $\text{CrOOH}$  acting as an acid. A number of these chromites are found in nature, chief among them being the ferrous salt, *chrome iron ore* ( $\text{Fe}(\text{CrO}_2)_2$ ).

**Chromic acid ( $\text{H}_2\text{CrO}_4$ ); the chromates.** When any of the compounds of chromium so far mentioned are heated *with an alkali* (or alkaline carbonate), oxygen is absorbed from the air and the chromium becomes hexavalent, forming salts of *chromic acid* ( $\text{H}_2\text{CrO}_4$ ). With iron chromite the reaction is represented in the equation



In formula and crystalline form the chromates are analogous to the sulfates and manganates. Most of them are of some shade of yellow, unless the base present contributes a color of its own to the salt. Of the chromates the potassium salt  $\text{K}_2\text{CrO}_4$  and the sodium salt  $\text{Na}_2\text{CrO}_4 \cdot 10 \text{H}_2\text{O}$  are the best-known soluble representatives. The insoluble lead chromate ( $\text{PbCrO}_4$ ) is the pigment known as *chrome yellow*. The insoluble barium salt  $\text{BaCrO}_4$  is of a lighter shade of yellow and is also used as a pigment.

The free chromic acid cannot be prepared in pure condition, owing to its tendency to lose water, with the formation of various condensed soluble acids, the chief of which is *dichromic acid* ( $\text{H}_2\text{Cr}_2\text{O}_7$ ). These also lose water readily, finally forming the trioxide  $\text{CrO}_3$ , which crystallizes in deep red needles, very soluble in water but much less so in sulfuric acid. Consequently, when concentrated sulfuric acid is added to a chromate, it is this anhydride which is obtained and not one of the chromic acids:



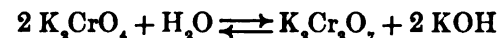
**Dichromic acid ( $\text{H}_2\text{Cr}_2\text{O}_7$ ); the dichromates.** Unlike sulfuric acid, chromic acid forms no acid salts. Reactions which might be expected to produce such salts lead instead to salts of various condensed acids, the chief of which is *dichromic acid* ( $\text{H}_2\text{Cr}_2\text{O}_7$ ). Thus, when the calculated quantity of sulfuric acid acts upon a solution of potassium chromate, the dichromate crystallizes from the solution in the form of orange-red, triclinic crystals of

the composition  $K_2Cr_2O_7$ , the salt being analogous to potassium pyrosulfate ( $K_2S_2O_7$ ):

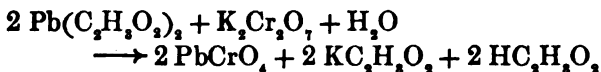


This salt is very soluble in hot water but only moderately soluble in cold. On account of its moderate solubility and easy purification by crystallization, this salt has long been used for all purposes to which a soluble derivative of chromic acid is suited. The sodium salt  $Na_2Cr_2O_7 \cdot 2 H_2O$  is very soluble and somewhat deliquescent, but the difficulties attending its preparation have been overcome, and for commercial purposes the sodium compound is now replacing the potassium salt.

When a solution of a dichromate is treated with an excess of alkali, the normal chromate is obtained, just as would be the case with an acid salt. Excess of acid converts the chromate once more into the dichromate, so that the condition in solution is one of equilibrium, as expressed in the equation

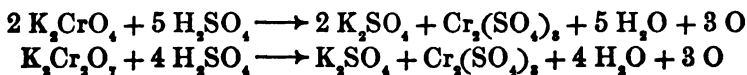


The anions of both chromate and dichromate are present in the solution, and when various salts are added, either a chromate or a dichromate may precipitate, depending upon which is the less soluble. For example, normal *lead chromate* is precipitated when a solution of a dichromate is treated with a lead salt:



**Oxidizing action of the chromates.** Owing to the fact that chromium, like manganese, can readily *diminish in valence and play the part of a base-forming element*, both the chromates and the dichromates are good oxidizing agents.

In the presence of an acid — for example, sulfuric acid — the oxidation reaction is represented in the equations



## CHAPTER XLII

### THE VANADIUM AND MOLYBDENUM FAMILIES; RADIOACTIVITY

**General.** The elements constituting the vanadium and molybdenum families are all typical *metallo-acid elements* (p. 683). In the free state all of these elements are *metals* of rather high density and characteristic properties. In combination, and *under strong reducing conditions*, they all play the part of a positive metallic ion. *Under oxidizing conditions* they all increase in valence and form acids.

In a general way, therefore, the chemistry of all these elements resembles that of manganese and chromium, the latter element being, indeed, a member of the molybdenum family, but for purposes of convenience considered along with manganese.

### THE VANADIUM FAMILY

**General.** The three elements, vanadium, columbium, and tantalum, constitute a family in the group with phosphorus. The second one was named columbium, in honor of America, since it was discovered in a mineral from Connecticut. It was rediscovered as an impurity in tantalum and renamed niobium (Niobe being the daughter of Tantalus), and both names are in use.

**Vanadium.** Vanadium was first described as a new element by Sefström in 1830, and named in honor of Vanadis, the Scandinavian goddess of fortune. It is much the most abundant of the three and is widely distributed in nature, but it is nowhere concentrated in very rich deposits. *Vanadinite* ( $3\text{Pb}_3(\text{VO}_4)_2 \cdot \text{PbCl}_2$ ) is the most widely distributed mineral, occurring as a covering of small, reddish crystals on other minerals. The ashes of nearly all anthracite coal contain vanadium in varying quantities. At present over half of the ore of

commerce is *patronite*, a complex sulfide of vanadium found in Peru. In the United States some ferrovanadium is made from *roscoelite* and *carnotite*, both minerals coming from Colorado.

**Preparation.** Metallic vanadium is very difficult to prepare, owing to the fact that it is reducible only at a very high temperature, and under these conditions it combines with most reducing agents and with nitrogen. It is most successfully prepared by reducing its oxide with *mixed metal* (p. 601).

**Properties and chemical conduct.** The pure metal is a brilliant, silvery substance, crystallizing in the hexagonal system like phosphorus. It is very hard and somewhat brittle, and has a density of about 6.02. It melts at 1720°. By reducing a mixture of the oxides of iron and vanadium an alloy called *ferrovanadium* containing about 30 per cent vanadium is obtained, the production in the United States being about 12,000,000 lb. annually. This alloy is used in the manufacture of vanadium steel, which is very tough and strong. This application constitutes the chief use for vanadium, though some of its compounds are employed as catalytic agents, as in the manufacture of certain dyes and of sulfuric acid. The metal is rather easily oxidized and is soluble in concentrated acids, forming metallic salts.

**Compounds of vanadium.** Compounds of vanadium, like those of chromium, are obtained by heating the ore with sodium carbonate and an oxidizing agent (p. 692), sodium vanadate ( $\text{Na}_2\text{VO}_4$ ) being formed in the reaction. When a solution of this salt is treated with an excess of ammonium chloride, the sparingly soluble ammonium metavanadate ( $\text{NH}_4\text{VO}_3$ ) is precipitated:



When this salt is heated, the pentoxide  $\text{V}_2\text{O}_5$  is obtained, and from this other compounds can be made. Many of these are highly colored in shades of violet, blue, green, red, and yellow. The great majority of the derivatives of vanadium are complexes, sometimes of very complicated formulas.

**Columbium and tantalum.** These two elements are usually, though not always, found together in nature in the form of columbates and tantalates. Minerals containing them are found in many localities, especially in the United States, but they are very local and never occur in large deposits. *Columbite*, the mineral in which they were first discovered, is essentially an

iron and manganese salt of the mixed acids  $\text{HCbO}_3$  and  $\text{HTaO}_3$ , and is much richer in columbium than in tantalum. *Tantalite*, chiefly of the composition  $\text{Fe}(\text{TaO}_3)_2$ , always carries some columbium.

**Preparation and properties.** The metals are obtained by the method described in connection with vanadium, columbium being much the more difficult to prepare in a pure state. Tantalum resembles platinum in appearance and is about as hard as wrought iron. It is more ductile than columbium and can be drawn to wires only 0.03 mm. in diameter. Its density is 16.6 and its melting point  $2900^\circ$ . It is inactive toward alkaline solutions and toward acids other than hydrofluoric. At a low red heat it burns in the air.

The ductility of tantalum and its very high melting point make it well adapted to serve as a metallic filament in incandescent lamps. It was the first metal to be so employed; but before tantalum lamps had been used to any great extent they were superseded by tungsten lamps, tungsten being much easier to secure in the pure state than tantalum and having a higher melting point.

**Compounds of the elements.** The compounds of columbium and tantalum are for the most part very complex. The simplest ones are the oxides and the various halogen derivatives, particularly the fluo-acids and their salts. These acids have different formulas, namely,  $\text{H}_2\text{CbF}_6\text{O}$  and  $\text{H}_2\text{TaF}_7$ , and the different solubility of salts of these two acids affords the best means of separating the two elements.

## THE MOLYBDENUM FAMILY

**General characteristics.** The elements which follow chromium — namely, molybdenum, tungsten, and uranium — are rather more abundant in nature than those of the preceding group. As elements they are metals of high melting point and density. Molybdenum and tungsten are almost entirely acid-forming in chemical conduct, while uranium combines both acid-forming and base-forming qualities. Like chromium they are usually hexavalent, and many of their compounds have formulas similar to those of chromium.

**Molybdenum.** The Greek word from which *molybdenum* is derived was applied in early writings to many substances having a superficial resemblance to lead — among others to a mineral resembling graphite, which is now called *molybdenite*. In 1778 Scheele showed that from this mineral a new oxide could be

obtained, which he called molybdic acid. The element occurs chiefly in *molybdenite* ( $\text{MoS}_2$ ), in *wulfenite* ( $\text{PbMoO}_4$ ), and in *molybdic ocher*, a hydrated molybdate of iron. Its ores are nowhere very abundant and usually require much concentration before they are suitable for metallurgical purposes. They are produced in Canada, Arizona, Colorado, and Norway.

**Preparation and properties.** Molybdic oxide ( $\text{MoO}_3$ ) can be reduced by hydrogen to the state of a fine metallic powder, but the compact form of the metal is obtained by reduction with aluminium or, better, with *mixed metal*. It is a moderately heavy, silvery metal, of density 8.6, melting only at a white heat. It is too volatile to serve as a filament for lamps, but in the form of a fine wire it is used as a support for tungsten filaments. *Ferromolybdenum* is made in the same way as *ferrovanadium* and is used for making alloy steel for high-speed tools and gun barrels.

**Compounds.** Molybdenum forms a great variety of oxides, ranging from the monoxide  $\text{MoO}$  to the trioxide  $\text{MoO}_3$ . The latter is a nearly white, crystalline compound, which is rather easily volatile and is frequently called molybdic acid. The simple molybdates derived from it have formulas like the chromates — for example, the potassium salt  $\text{K}_2\text{MoO}_4$  — but usually the salts are derived from condensed acids, ammonium molybdate having the formula  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4 \text{H}_2\text{O}$ .

Compounds of molybdenum are used for blue colors in porcelain painting, in coloring leather, and also in dyeing.

**Complex acids.** When molybdic acid is brought into contact with soluble salts of phosphoric acid, especially in the presence of nitric acid, various complex salts are deposited, the formulas of which are very complicated. They are usually expressed by writing the formulas of the anhydrides of both acids and base, as shown in the formula for ammonium phosphomolybdate,  $3 (\text{NH}_4)_2\text{O} \cdot \text{P}_2\text{O}_5 \cdot 22 \text{MoO}_3 \cdot 12 \text{H}_2\text{O}$ . Similar salts are formed, in which the  $\text{P}_2\text{O}_5$  and the  $\text{MoO}_3$  are replaced by a number of different anhydrides, such as  $\text{As}_2\text{O}_5$ ,  $\text{I}_2\text{O}_5$ ,  $\text{Ta}_2\text{O}_5$ ,  $\text{V}_2\text{O}_5$ ,  $\text{WO}_3$ ,  $\text{UO}_3$ , and many others. The ratios are sometimes very complicated, and nothing is known about the way in which these compounds are made up; yet they are often very

beautifully crystallized and appear to be perfectly definite chemical compounds. The ammonium salt, whose formula is given above, is a yellow, crystalline precipitate, insoluble in nitric acid, and advantage is taken of its formation in the separation and estimation of phosphoric acid. This constitutes an important use for molybdenum.

**Tungsten.** The element tungsten was discovered by Scheele as a constituent of a mineral now called *scheelite* ( $\text{CaWO}_4$ ). This mineral and *wolframite* ( $\text{FeWO}_4$ ) are not very rare in nature, and considerable quantities of the ore are produced annually. China produces the most ore, then Colorado, California, and Bolivia. The compounds of tungsten are easily extracted from the ore. It is not difficult to reduce the oxide to the metallic state, but a powder is obtained which it is almost impossible to melt to a compact ingot. It is best prepared like vanadium; or the powdered metal can be dissolved in mercury and cadmium, the amalgam fashioned into wire, and the other metals expelled by electrical heating, leaving the pure, coherent tungsten. A similar result can be attained by pressing the powder into the form of a wire and rolling or hammering it at a high temperature, maintained by electrical heating. It is a very hard metal, as ordinarily produced, but by the proper mechanical treatment it can be obtained in a malleable and very ductile state resembling platinum. It has a very high melting point ( $3400^\circ$ ), is a good conductor, and does not oxidize very readily in the air. It is of much value for spark points for automobiles, electrical contacts for large currents, and filaments in incandescent lamps. Tungsten is used as an important alloy metal for steels, particularly for armor plate and for tools. Tungsten steel holds its temper at a red heat, so that with tools of this alloy a lathe can be driven at a very high speed without injury to the tool. It is a constituent of some other alloys such as stellite (p. 689).

**Tungsten lamp.** The efficiency of any material as a filament in an incandescent lamp depends primarily upon its conductivity and its melting point. Other conditions being the same, most substances are equally incandescent at a given temperature, and the higher the temperature the more brilliant the light they give. Tungsten not only has the highest melting

point of all the metals but it has practically no vapor pressure at a white heat. It is a good conductor, so that to secure sufficient resistance it is necessary to use a wire that is very fine as well as rather long. This necessitates looping the wire and supporting it at frequent intervals to prevent sagging. While carbon does not melt at any attainable temperature, it has considerable vapor pressure at a white heat so that it is not practicable to heat a carbon filament above a bright yellow glow. The relative efficiency of some common types of lamps is approximately as follows:

Ordinary carbon filament . . . . .	3.25 watts per candle power
Graphitized carbon filament (Gem). . . . .	2.50 watts per candle power
Tantalum filament . . . . .	2.00 watts per candle power
Tungsten filament . . . . .	1.30 watts per candle power
Nitrogen filled (tungsten) . . . . .	0.75 watts per candle power

**Compounds of tungsten.** In a general way the compounds of tungsten resemble those of molybdenum. A few form valuable pigments; sodium tungstate ( $\text{Na}_2\text{WO}_4$ ) is used as a "fireproof" coating for cloth, and also as a mordant in the dyeing industry. Phosphotungstic acid (analogous to phosphomolybdic acid) is used as a reagent in the detection of certain alkaloids.

**Uranium.** Uranium was discovered by Klaproth, in 1789, in the mineral known as *pitchblende*; it was named in honor of the planet Uranus, which had been discovered only a short time before. It is found in quite a number of complex minerals associated with lead, vanadium, thorium, and the rare earths. Of these, *uraninite*, or *pitchblende* ( $\text{U}_3\text{O}_8$ ), is the most common, the ore sometimes carrying from 75 to 85 per cent uranium. Joachimstal, in Bohemia, leads in the production of this mineral. *Carnotite*, essentially a vanadate of uranium and potassium ( $\text{K}_2\text{O} \cdot 2\text{UO}_3 \cdot \text{V}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$ ), is produced in Colorado and Utah.

**Properties and conduct.** Uranium is a somewhat malleable metal resembling nickel in appearance. It oxidizes slowly in the air and is soluble in the ordinary acids, forming salts. Its density is 18.7 and it melts above  $1850^\circ$ . As an acid-forming element it resembles chromium, forming salts of the formulas  $\text{M}_2\text{UO}_4$  and  $\text{M}_2\text{U}_2\text{O}_7$ , but ordinarily it plays the part of a base-forming element. In this capacity it forms a great variety of

salts, the best known of which are a series in which the radical  $\text{UO}_2$ , known as *uranyl*, acts as a bivalent metal. Examples of these are uranyl nitrate ( $\text{UO}_2(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ ) and uranyl acetate ( $\text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2 \text{H}_2\text{O}$ ).

Compounds of uranium are used in glass making to produce a yellowish-green, fluorescent glass, and in china painting to secure a velvety black color. Uranium steels are also made.

### RADIOACTIVITY

**Radioactivity of uranium.** In 1896 the French physicist Becquerel discovered that uranium, as well as its compounds, possesses a property which is called *radioactivity*. A photographic plate wrapped in black paper and placed near these substances is affected as though exposed to light. A charged electrometer is rapidly discharged when in the neighborhood of any of them, showing that the air all about them is made a conductor.

Fig. 178 represents a simple form of aluminium-leaf electrometer, the leaves assuming the position indicated at *B* when an electric charge is communicated to the knob *A*.

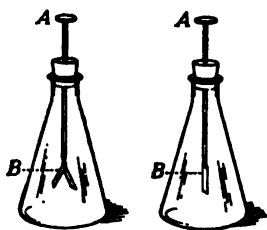


FIG. 178

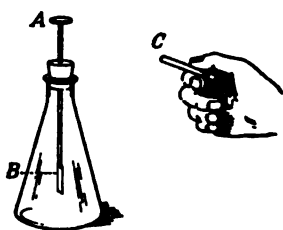


FIG. 179

When a substance containing uranium (Fig. 179, *C*) is brought near the knob, the charge is rapidly lost, and the leaves collapse as shown at *B*.

In the case of pure compounds the effect is proportional to the quantity of uranium present in the

salts, and is independent of their chemical character. The minerals containing uranium, notably pitchblende, are much more radioactive than the pure metal. This suggested that the property of radioactivity might possibly be due to some other substance contained in the ore and carried over into uranium compounds as an impurity.

**Discovery of radium.** Accordingly, Monsieur and Madame Curie made a careful study of pitchblende, in the hope of discovering some unknown element in it. They found that the barium chloride obtained from the mineral (amounting to about 30 pounds per ton) was exceedingly radioactive, and by a long-continued process of fractional crystallization they isolated a minute quantity of the chloride and bromide of a new element, to which they gave the name *radium*. These compounds are about three million times as radioactive as uranium. The spectrum of this element, its atomic weight (226), and its chemical properties place it in the second group as a homologue of barium, which it very closely resembles. The metal itself, isolated by Madame Curie in 1910, is very similar to barium in its reactions and appearance.

**Disintegration of radium.** The fact which gives radium its peculiar interest is that, although it is a well-characterized element, *it is unstable*. It is slowly undergoing a change which results in its own disappearance and in the emission of three types of rays, designated as alpha ( $\alpha$ ), beta ( $\beta$ ), and gamma ( $\gamma$ ) rays (p. 346). The alpha rays are *atoms of helium* each bearing two positive charges of electricity. They are shot off with a velocity of about 30,000 kilometers per second, but are stopped by a sheet of paper and cannot penetrate even very thin sheets of metal. The beta rays are *electrons* and are shot off with a velocity about equal to that of light. They are the same as cathode rays, but move much faster. They have greater penetrating power than the alpha rays but are stopped by relatively thin sheets of metal. The gamma rays are identical in character with the X rays, consisting of very short ether waves. They can penetrate relatively thick layers of metals.

**Demonstration of the three types of rays.** The existence of these three types of rays can be shown in the following way: A small quantity of a material containing radium is placed in the bottom of a hole bored in a piece of lead (Fig. 180, A). A photographic plate B is fixed at some distance above the radium, and a magnetic field is created in the space

between by an electromagnet *C*. The rays from the radium are shot out of the hole like bullets from a rifle. The positive (alpha) rays are bent out of their course by the negative pole, while the negative (beta) rays are deflected by the positive pole. The gamma rays are not deflected.

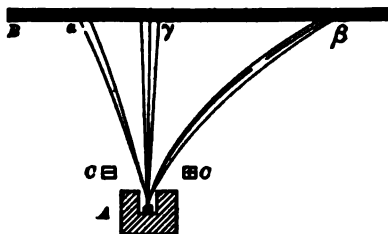


FIG. 180

By developing the photographic plate the extent of the deflection of the alpha and beta rays can be measured, and from such measurements it is possible to draw conclusions as to the relative masses and charges of the two kinds of particles.

**Origin of radium.** Radium is decomposing at a rate which places the average life of any quantity of it at about 2500 years, yet it is found in ores that are undoubtedly much older than this. It must therefore be in the process of formation from some other element. The labors of many chemists, particularly of Rutherford and Soddy, leave no doubt that this element is *uranium*. Radium is found in all ores of uranium and in no other ores, and the ratio between the radium present and the uranium is *exceedingly constant*, being 1 part of radium to 2,940,000 parts of uranium. It is also independent of the nature of the ore. This constant ratio merely represents the equilibrium between the rate at which uranium disintegrates and that at which radium disintegrates. Since this is so, it is clear that we cannot hope to find any deposits of radium richer than those afforded by uranium ores.

**Energy of radium.** During the disintegration of radium a great deal of energy is given off. Both the helium atoms and the electrons are shot off with very high kinetic energy, and the radium compound is kept heated by the energy set free. It is estimated that 1 g. of radium *hourly* evolves 132 cal. of heat. From this value, together with the average life period (2500 years) it is easy to calculate that the *total* energy given off by 1 g. of radium will be something like 250,000 times the heat of combustion of 1 g. of carbon.

This calculation gives us some idea of the small fraction of the total energy of an element that is liberated during chemical action; for in its ordinary reactions radium is not remarkable for its heat evolution compared with other elements. The steady evolution of heat by radioactive substances is held by some to be a very plausible explanation of the origin of the interior heat of the earth, and possibly that of the sun as well.

**Effects produced by radium.** By virtue of the energy liberated, or of the particles shot off at tremendous velocities, radium exerts a great influence upon other substances. It affects silver salts as exposure to light does; it produces fluorescence in many substances, such as barium platinocyanide, zinc sulfide, the diamond, and a number of other gems; it discolors the glass of bottles in which it is preserved, apparently by inducing chemical changes in the glass; it sterilizes seeds and kills many microorganisms, or at least diminishes their vitality. It is this last property which suggests its use in medicine as a cure for malignant diseases such as cancer, and experiments are being actively pushed to ascertain its value in this connection.

**Production and uses of radium.** Since radium is found only in uranium ores (which are themselves rare), and in exceedingly small quantities in them, it is clear that the total quantity of radium at present known to exist is very small, and that it is not likely to become any more available in the future. In 1 ton of pitchblende of 60 per cent uranium, there is about 0.2 g. of radium. At present it sells for \$125,000 per gram, calculated as metallic radium content. In the United States all radium is produced from carnotite, and the total production up to 1921 has been about 115 grams. Of this, 35 grams was produced in 1920.

Until recently nearly all the production has been sold to hospitals and physicians for medical purposes, and to scientific investigators. At present the larger percentage of the production is used in the manufacture of luminous enamels, where it is permanently lost. A limited quantity of residues of low radium content is sold for use as a fertilizer. From a scientific point

of view the most important use of radium is in scientific investigations, for we have gained invaluable knowledge from its study. In view of the extremely limited supply of radium and of its great importance to science, it is to be regretted that any should be permanently lost.

**The uranium series.** The work of many investigators, particularly of Rutherford and of Soddy, has shown that the disintegration of uranium is a very complicated process and takes place in many stages. At each stage either an electron or a helium atom is expelled (in rare cases both) and a new element is formed. This in turn undergoes a similar decomposition, radium being the fifth in order from the parent element uranium.

The final element formed, beyond which no change can be traced, is lead. Since the atomic weight of uranium is 238.2 while that of lead is 207.2, there is a loss of 8 helium atoms in the process. And since each helium atom carries with it two positive charges, there is an equivalent loss of negative charges, namely 16 electrons. The table gives the details of these changes, in the order of their occurrence.

TABLE OF URANIUM SERIES

ELEMENT	ATOMIC WEIGHT	AVERAGE LIFE	CHARACTER OF RAYS	PERIODIC FAMILY
Uranium 1 . . . .	238	$8 \times 10^8$ years	Helium	VI (A)
Uranium X . . . .	234	35.4 days	Electron	IV (A)
Uranium $X_2$ . . . .	234	1.65 minutes	Electron	V (A)
Uranium 2 . . . .	234	$8 \times 10^8$ years (?)	Helium	VI (A)
Ionium . . . . .	230	$2 \times 10^8$ years (?)	Helium	IV (A)
Radium . . . . .	226	2440 years	Helium	II (A)
Nitron . . . . .	222	5.55 days	Helium	0
Radium A . . . .	218	4.8 minutes	Helium	VI (B)
Radium B . . . .	214	38.5 minutes	Electron	IV (B)
Radium C . . . .	214	28.1 minutes	Electron	V (B)
Radium $C^1$ . . . .	214	$10^{-6}$ seconds	Helium	VI (B)
Radium D . . . .	210	24 years	Electron	IV (B)
Radium E . . . .	210	7.2 days	Electron	V (B)
Radium F . . . .	210	196 days	Helium	VI (B)
End-product . . . .	206			IV (B)

**Other radioactive series.** Very soon after the discovery of the radioactivity of uranium it was found that the element *thorium* is similarly radioactive, giving rise to a series of elements resembling those derived from uranium. One of these, *mesothorium*, is produced commercially to replace radium in its applications. A third element, *actinium*, was also found that is radioactive, and gives rise to a shorter series, but it is believed to be a product of a side decomposition of one of the uranium series. Potassium and rubidium have been found to possess some radioactivity, but not much is known about this.

**Isotopic elements; isotopes.** In 1910 Soddy called attention to the fact that some of the decomposition products of these several elements have chemical properties that are indistinguishable from those of well-known elements or from each other, and a mixture cannot be separated, though the atomic weights are different.

It will be remembered that each succeeding group in the periodic table increases in positive valence and decreases in negative valence as we pass from Group I to Group VII; and that the average difference in weight between consecutive elements is about 2. Soddy pointed out that, when a radioactive element loses an  $\text{He}^{++}$  atom of atomic weight 4, the chemical properties of the element produced should be those belonging to the second periodic group *below* the original position of the element (a decrease of two positive valences); and when it loses an electron the place of the new element should be one group *in advance* of the old place (a decrease of one negative valence).

Since the products of decomposition sometimes lose a helium atom and sometimes an electron, the path of decomposition across the periodic table is a zigzag and frequently brings several products of decomposition into nearly the same position in the table, with atomic weights close together. An inspection of the last column of the table (p. 706) will make this clear. Also products from the three different series often fall into the same periodic position. Thus radium and thorium X fall in the same family

and have atomic weights of 226 and 224; ionium and thorium fall in the same family, with atomic weights of 230 and 232.15. In all chemical properties such pairs of elements are *identical*. The two elements are called *isotopes*, or *isotopic elements*.

**End-point of the series.** A study of the three series that have been mentioned has shown that they all reach an inactive end-point close together in atomic weight and near the position occupied by lead, so that all the end-products are isotopic with lead. The end-product of the uranium series has an atomic weight of 206; that of the thorium series an atomic weight of 208.4; while the atomic weight of lead is 207.2.

Now lead is always found in the ores of both uranium and thorium, and most careful work by a number of chemists (notably by Richards) has shown that the lead isolated from these ores has a different atomic weight from ordinary lead, the values ranging from 206.08 to 207.69.

The density of this lead from radioactive sources was also found to be different from that of ordinary lead. For example, Richards found lead obtained from Norwegian cleveite to have a density of 11.273, while that of ordinary lead is 11.3416.

**Elements with fractional atomic weights.** The fact that at least three isotopes of lead are known, each with its own atomic weight, has suggested that possibly some of the elements whose weights differ notably from whole numbers may be in reality constant mixtures of isotopes. Of the elements having atomic numbers of from 1 to 30, the atomic weights of neon, magnesium, silicon, and chlorine are the most irregular.

Experimental evidence indicates strongly that neon is a mixture of isotopes of atomic weights 20 and 22. By electrical methods Dempster in 1920 proved magnesium to be a mixture of three isotopes of weights 24, 25, and 26. By diffusion of hydrogen chloride Harkins in the same year obtained evidence that chlorine is also a mixture of isotopes.

**Definition of an element.** The facts of radioactivity make it a difficult matter to frame a satisfactory definition of an element.

It serves every practical purpose to think of an element as a substance that cannot be resolved into two or more substances of different compositions. Under this definition a mixture of the isotopes of lead constitute one element.

At the same time it must be recognized that the atom of each element is a structure, and that under conditions about which we know very little, this structure may spontaneously change or be knocked to pieces, producing other kinds of atoms. We accord a place in the periodic table to such elements as have a high degree of permanence and give the typical X-ray spectrum that determines the atomic number (p. 345). Most of the decomposition products of uranium and thorium do not meet these tests and are isotopes of other stable elements.

### QUESTIONS

1. Define a metallo-acid element.
2. Do the metallo-acid elements occur in nature in oxidized or in reduced form? What conclusion do you draw as to the prevailing conditions during the formation of minerals?
3. If a mineral containing vanadium in tervalent form were to be found, would you consider it probable that it is a primitive mineral or one formed by secondary alterations?
4. What metals form vitriols? What are the characteristics of these salts?
5. From the formula of pitchblende, what inferences would you draw as to the valence of uranium in this compound?
6. What is the advantage of a high-speed tool?
7. Do you think that cloth can be made really fireproof?
8. Make a list of the elements that form tetrachlorides.
9. Vanadium steel usually contains only a mere trace of vanadium. Why is it called vanadium steel?

### PROBLEMS

1. From the formula of carnotite, what percentage of uranium should it contain if pure?
2. What weight of radium is present in a ton of pure carnotite?

## CHAPTER XLIII

### GOLD AND THE PLATINUM FAMILY

	ATOMIC WEIGHT	DENSITY	MELTING POINT	HIGHEST OXIDE	HIGHEST CHLORIDE
Ruthenium (Ru) . . . . .	101.7	12.30	2450° (?)	RuO <sub>4</sub>	RuCl <sub>4</sub>
Rhodium (Rh) . . . . .	102.9	12.44	1950°	RhO <sub>3</sub>	RhCl <sub>3</sub>
Palladium (Pd) . . . . .	106.7	11.40	1550°	PdO <sub>2</sub>	PdCl <sub>4</sub>
Osmium (Os) . . . . .	190.9	22.50	2700° (?)	OsO <sub>4</sub>	OsCl <sub>4</sub>
Iridium (Ir) . . . . .	193.1	22.41	2350° (?)	IrO <sub>3</sub>	IrCl <sub>4</sub>
Platinum (Pt) . . . . .	195.2	21.50	1755°	PtO <sub>2</sub>	PtCl <sub>4</sub>
Gold (Au) . . . . .	197.2	19.32	1063°	Au <sub>2</sub> O <sub>3</sub>	AuCl <sub>3</sub>

**General.** The periodic arrangement places gold along with copper and silver in the first group of elements, but it is much more closely related to the platinum metals and will be considered along with them.

The eighth group in the periodic arrangement differs very much in character from the others, and is made up of three sets of elements, each consisting of three members. The first of these, comprising iron, cobalt, and nickel, has been described in a previous chapter. The six members of the other two sets, including ruthenium, rhodium, palladium (with atomic weights of approximately 100), and osmium, iridium, and platinum (with atomic weights lying near the value 200), are very closely related to each other and are known collectively as the *platinum metals*.

### GOLD

**Occurrence.** From the earliest times gold has been known as a precious metal. It was called *aurum* by the Romans, and from this name the symbol Au is derived. For the most part it is found in nature in the native state, either embedded in quartz

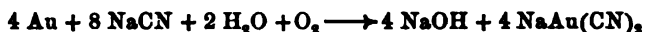
veins or as grains or large nuggets in the heavy sands derived from them. In this state it is usually alloyed with smaller quantities of other metals, such as silver, copper, and lead. In combination it occurs as a constituent of a number of minerals, nearly all of which contain tellurium, together with silver and some copper. A little gold telluride is apparently dissolved in the sulfides of many other metals, such as those of copper, lead, and silver, so that gold is obtained as a by-product in the refining of these metals. The Transvaal is the largest producer of gold. In the United States it is found in Alaska and in a number of the states in the union, California, Colorado, and Nevada leading in its production. The United States produces about one fifth of the world's supply. The total output of gold greatly decreased during the World War, falling from \$470,500,000 in 1915 to \$373,000,000 in 1918. This decrease was due primarily to the fact that, while the price of other metals increased, gold, being the basis of international credit, remained stationary in price; namely, \$20.67 per ounce.

**Mining and extraction.** Native gold is obtained in crude form by *placer* mining. The sand containing the gold is shaken or stirred in troughs of running waters, called *sluices*. This sweeps away the sand but allows the heavier gold to sink to the bottom of the sluice. Sometimes the sand containing the gold is washed away from its natural location into the sluices by powerful streams of water delivered under pressure from pipes. This is called *hydraulic* mining. In *vein* mining the gold-bearing quartz is stamped into fine powder in stamping mills, and the gold is extracted by a number of processes, two of which will be described.

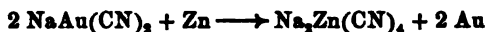
1. *Amalgamation process.* In the amalgamation process the powder containing the gold is washed over a series of copper plates whose surfaces have been amalgamated with mercury. The gold sticks to the mercury or alloys with it, and after a time the gold and mercury are scraped off and the mixture is distilled. The mercury distills off and the gold is left in the retort ready for refining.

2. *Cyanide process.* This process depends upon the fact that gold is soluble in a solution of sodium cyanide in the presence of the oxygen of the air.

The powder from the stamping mills is treated with a very dilute sodium cyanide solution which extracts the gold:



From this solution the gold can be obtained by electrolysis or by precipitation with metallic zinc:



**Refining of gold.** Gold is refined by three general methods:

1. *Electrolysis.* When gold is dissolved in a solution of sodium cyanide and the solution electrolyzed, the gold is deposited in very pure condition on the cathode.

2. *Cupellation.* When the gold is alloyed with easily oxidizable metals, such as copper or lead, it may be refined by cupellation. The alloy is fused with an oxidizing flame on a shallow hearth made of bone ash, which substance has the property of absorbing metallic oxides but not the gold. Any silver which may be present remains alloyed with the gold.

3. *Parting with sulfuric acid.* Gold may be separated from silver, as well as from many other metals, by heating the alloy with concentrated sulfuric acid. This dissolves the silver, while the gold is not attacked. Sometimes nitric acid is used instead of sulfuric acid.

**Properties.** Gold is a yellow metal of density 19.32. It melts at about the same temperature as copper ( $1063^\circ$ ) and boils at approximately  $2500^\circ$ . It is about as soft as silver, is a good conductor of electricity, and is the most ductile and malleable of all the metals. It forms alloys with most of the metals, and its uses are too familiar to require description. In a pure condition gold is too soft to be used for jewelry and coinage, and for such purposes it is always alloyed with copper or silver. The fineness of gold is usually expressed in terms of carats, 24-carat gold being pure, while 18-carat (75 per cent) is the grade used for the best jewelry. For coinage a 90 per cent alloy is used. The finest ruby-colored glass is produced by the addition of a little metallic gold, the color being due to the presence of gold in colloidal dispersion.

**Chemical conduct.** Gold is not attacked by any one of the common acids. It is easily dissolved by solutions containing free chlorine or bromine, by aqua regia, and by solutions of

sodium cyanide in the presence of air. Fused alkalis also corrode the metal, with the formation of aurates of the general type  $\text{KAuO}_2$ .

In its compounds gold nearly always acts as a trivalent element. Auric hydroxide  $(\text{Au}(\text{OH})_3)$  yields two series of compounds. The one is represented by such salts as the chloride  $\text{AuCl}_3$ , while the other consists of aurates, such as potassium aurate  $(\text{KAuO}_2)$ . Gold forms a number of sulfides, such as the monosulfide  $\text{Au}_2\text{S}$  and the trisulfide  $\text{Au}_2\text{S}_3$ . Like the sulfides of arsenic, antimony, and tin, these are soluble in ammonium polysulfide, with the formation of thio salts.

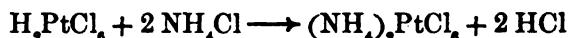
**Complex compounds.** The great majority of the compounds of gold are complex compounds, such as cyanides and ammonia derivatives. Among the most important is *chlorauric acid*  $(\text{HAuCl}_4)$ , formed by dissolving gold in aqua regia. The sodium salt  $(\text{NaAuCl}_4 \cdot 2\text{H}_2\text{O})$  is used as a toning reagent in photography. The cyanides  $\text{KAu}(\text{CN})_2$  and  $\text{KAu}(\text{CN})_4$  are used as electrolytes in gold plating. One of the most characteristic reactions of gold compounds is the production of a purple precipitate known as the *purple of Cassius*, when a solution containing stannous chloride and stannic acid is warmed with a very dilute solution of a gold salt. The gold salt is reduced by the stannous chloride, and colloidal gold is precipitated along with colloidal stannic acid.

## PLATINUM

**History and occurrence.** The element *platinum* owes its name to the Spanish word *platina*, which is a diminutive of the word *plata*, "silver." It was first described with some care by Brownrigg in 1750. Platinum occurs in nature alloyed with various other metals belonging to the gold and platinum family, as well as with copper and iron. It is found chiefly in the Ural Mountains in Russia, smaller amounts being found in Brazil, Colombia, and the Pacific coast states. Like gold, it occurs in heavy sands, associated with magnetite, rutile, diamond, and quartz, and constitutes from 50 to 80 per cent of the crude alloy. A single well-defined mineral compound is known; namely, *sperrylite*  $(\text{PtAs}_2)$ . Some platinum is now recovered from the electrolytic mud of the gold and silver refineries.

In normal times Russia furnishes by far the largest amount of the metal. Thus, in 1914 that country produced 241,200 troy ounces out of a total world's production of 263,453. During the World War, this supply was cut off while at the same time the demand for platinum, especially for use as a catalyzer in the production of sulfuric acid and other chemicals, greatly increased. As a result, the price of the metal rose from about \$45 per troy ounce in 1914 to \$105 in 1918. Because of the importance of the metal for war purposes and because of its limited supply, the government restricted its use and at the same time purchased a considerable supply. At the close of the war the government sold its excess supply at \$105 per troy ounce, which is five times the price of gold.

**Preparation.** Native platinum is usually alloyed with gold and the platinum metals. To separate the platinum the alloy is dissolved in aqua regia, which converts the platinum into chloroplatinic acid ( $\text{H}_2\text{PtCl}_6$ ). Ammonium chloride is then added, which precipitates the platinum as insoluble ammonium chloroplatinate;



Some iridium is also precipitated as a similar compound. On ignition the double chloride is decomposed, leaving the platinum as a spongy metallic mass, which is melted in an electric furnace and rolled or hammered into the desired shape.

**Properties.** Platinum is a grayish-white metal of density 21.5, which melts at  $1755^\circ$ . It is very malleable and ductile. It is harder than gold and is a good conductor of electricity. In finely divided form it adsorbs gases, especially oxygen and hydrogen. Under these conditions, the gases are in a very active condition and will combine with each other at ordinary temperatures. Thus a jet of hydrogen or coal gas directed upon spongy platinum is at once ignited. Under ordinary conditions it is not attacked by the common acids, though hot, concentrated sulfuric acid slowly dissolves it. It is quite permanent in the air, and neither oxygen nor water vapor attacks it even at red heat. Free chlorine dissolves it, forming platinum tetrachloride ( $\text{PtCl}_4$ ). Aqua regia converts it into *chloroplatinic acid* ( $\text{H}_2\text{PtCl}_6$ ). Fused alkalis corrode it, forming platينات, especially in the presence of oxidizing agents such as nitrates. It alloys readily

with many easily reducible metals and is therefore attacked or dissolved when heated with compounds of such metals together with a reducing agent. Since hydrogen gas readily passes through sheet platinum when the latter is hot, it is not safe to heat in a gas flame any easily reducible oxide in a platinum crucible.

**Platinum as a catalytic agent.** Platinum is remarkable for its property of acting as a catalytic agent in a large number of chemical reactions, and mention has been made of this use of the metal in connection with the manufacture of sulfuric acid. When desired for this purpose some porous or fibrous substance, such as asbestos, is soaked in a solution of chloroplatinic acid and then ignited. The platinum compound is decomposed and the platinum deposited in very finely divided form. Asbestos prepared in this way is called *platinized asbestos*. For some reactions, as in the oxidation of ammonia by air (p. 262), the platinum is used in the form of a finely woven gauze. The catalytic action seems to be in part connected with the property of adsorbing gases and rendering them nascent. Some other metals possess this same power, notably palladium, which is remarkable for its ability to adsorb hydrogen.

**Applications.** The applications of platinum in the sciences and the industries depend largely upon its high melting point, its chemical inactivity, and its malleability and ductility. It is extensively used (1) in scientific laboratories and in certain industries for evaporating pans, catalytic materials, and a great variety of laboratory appliances; (2) in electrical apparatus for contact points; (3) in dentistry as pins for artificial teeth and as foil and plates in construction work; (4) in jewelry as a substitute for gold. Because of the limited supply of the metal and its fundamental importance in necessary industries, it is unfortunate and unreasonable that it should be used for jewelry.

The following rough estimate has been made of the amount of platinum produced and its uses: "Of the 5,000,000 or more ounces of platinum in existence, catalyzing processes have claimed 500,000 oz., dental uses 1,000,000 oz., chemical apparatus 1,000,000 oz., electrical devices 500,000 oz., and jewelry 500,000 oz."

**Platinum substitutes.** To meet the serious shortage of platinum, efforts are being made to discourage its use in jewelry and to provide substitutes for other uses. Tungsten is taking its

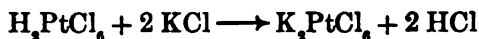
place for many purposes, especially for electrical spark contacts; wires of nickel iron coated with copper are now used in the manufacture of incandescent lamps; electrical-resistance heaters are made of alloys of nickel and chromium; quartz dishes are substituted for platinum in the industries; and a variety of alloys are being proposed for use in small laboratory utensils. Among these the following are the most promising at present:

Palau, an alloy of palladium (Pal) and gold (Au)

Rhotanium, an alloy of gold, palladium, and a small percentage of rhodium

Illium, essentially an alloy of nickel, chromium, copper, and molybdenum

**Compounds of platinum.** Like tin, platinum acts either as a bivalent or as a quadrivalent element, and the hydroxides corresponding to each valence can act either as acids or as bases. Some tervalent compounds are also known. In general, the oxygen derivatives of platinum, including the oxygen acids, as well as the platinates and platinites, are unstable and easily decomposed by heat. Its best-known compounds are its halogen derivatives, especially the salts of *chloroplatinic acid* ( $\text{H}_2\text{PtCl}_6$ ). This free acid, which forms reddish, deliquescent crystals of the composition  $\text{H}_2\text{PtCl}_6 \cdot 6 \text{H}_2\text{O}$ , is obtained by dissolving platinum in aqua regia. When added to a solution of potassium chloride, *potassium chloroplatinate* is formed as a reddish-yellow salt:



Sodium chloride and ammonium chloride act in the same way. The sodium salt, however, is soluble in dilute alcohol while the salts of potassium and ammonium are not, and this difference in property is taken advantage of in the separation of potassium and sodium from each other.

**Other platinum metals.** The other platinum metals—palladium, rhodium, ruthenium, osmium, and iridium—are all gray metals and have very high melting points and densities. They are found alloyed with native platinum. In chemical conduct they are like gold and platinum. Each one forms several series of compounds, in which the valence is either 2, 3, or 4; each

gives a variety of oxygen compounds of rather unstable character, and each forms more stable chloro acids and complex derivatives of ammonia and cyanogen. Nearly all of these compounds are highly colored in a great variety of tints.

**Palladium.** Palladium is the most abundant one of the five. It is obtained from native platinum and also from the electrolytic muds in the refining of certain nickel ores, especially those at Sudbury, Canada (p. 633). It is a soft metal closely resembling platinum in appearance, but of less density and of lower melting point. It is more pronouncedly basic than the others, dissolving in concentrated acids, especially in nitric acid, and forming a number of bivalent and moderately stable oxygen salts, such as the nitrate  $\text{Pd}(\text{NO}_3)_2$  and the sulfate  $\text{PdSO}_4$ . As an elementary substance its most remarkable property is its capacity for adsorbing large volumes of hydrogen. When the metal is finely divided, this may amount to as much as eight hundred volumes, and an even larger volume is adsorbed when an electrode is covered with the spongy metal and is made the cathode in the electrolysis of a dilute acid solution. The hydrogen so adsorbed is in a very active state, showing the reactions appropriate to its position in the electrochemical series. For example, such a charged electrode, dipped into a solution of copper salt, at once precipitates copper.

Palladium is used in making graduated vernier scales and as a substitute for platinum in jewelry. While it commands about the same price as platinum, it is only half as heavy, so that a given weight will go twice as far. It is also used as a catalyzer in industrial reactions, as in the reduction of certain fats and oils.

**Rhodium.** Rhodium resembles aluminium in appearance. Of all these metals, it is the most easily attacked by free chlorine, but it is exceedingly resistant to the action of acids.

**Ruthenium.** Ruthenium is hard and brittle, and is dark gray or nearly black in color. It forms a variety of oxygen compounds, the formulas of which recall those of manganese—for example,  $\text{RuO}_2$ ,  $\text{K}_2\text{RuO}_4$ , and  $\text{KRuO}_4$ . It also forms a volatile oxide of the formula  $\text{RuO}_4$ . This is produced by the oxidizing action of aqua regia, and is possibly formed by heating the metal in the air. It is a yellow compound, which melts at about  $26^\circ$ , boils at about  $100^\circ$ , and is volatile with steam.

**Osmium.** Osmium is interesting as being the heaviest of all known substances, having a density of 22.5. It is very hard and infusible, and is chiefly acid-forming in character. It forms an oxide ( $\text{OsO}_4$ ) which resembles the corresponding oxide of ruthenium. This oxide is volatile with steam and is formed by the action of aqua regia upon osmium. It is often present in the steam arising when solutions of crude platinum salts are boiled,

and has a very irritating and unpleasant odor. It is called *osmic acid*, though it has no acid properties, nor does it form an acid with water. The name was given on account of its corrosive action, which it owes to oxidizing and not to acid properties. In acting as an oxidizing agent it deposits metallic osmium in very finely divided form, and this is a great irritant when deposited in sensitive tissues. It is used in biological laboratories as a hardening agent and as a stain in the preparation of microscopic sections.

**Iridium.** This element owes its name to the variety of colors seen during its chemical transformations. It is a silver-white metal, hard and brittle. It is often present in the platinum of laboratory vessels, making the latter harder and less subject to chemical corrosion. The standard meter bar preserved at Sèvres is an alloy of platinum and iridium. The residue obtained when native platinum is digested with aqua regia is essentially an alloy of iridium and osmium. It can be worked up into a very hard alloy called iridosmine, which is used as a material for pointing gold pens.

### QUESTIONS

1. Account for the fact that gold and platinum seldom are found in nature in the form of compounds.
2. Since gold is so much cheaper than platinum, why not use it in place of the latter element for the manufacture of laboratory utensils?
3. What precautions should one take in using a platinum crucible for laboratory purposes?
4. What compound is formed by the action of aqua regia upon each of the following metals: zinc, iron, aluminium, gold, platinum?
5. For what reactions has platinum been used as a catalyzer?
6. What metal is lightest? What one is heaviest?
7. Would you expect an 18-carat gold ring to be attacked by nitric acid?

### PROBLEMS

1. What weight of chlorauric acid can be prepared from 5 g. of 18-carat gold?
2. A piece of pure platinum foil weighing 8 g. was dissolved in aqua regia, and the solution was evaporated to dryness. Calculate the weight of the residue.
3. Ammonium chloroplatinate is reduced to metallic platinum on heating. What weight of the metal will 100 g. of the salt yield?

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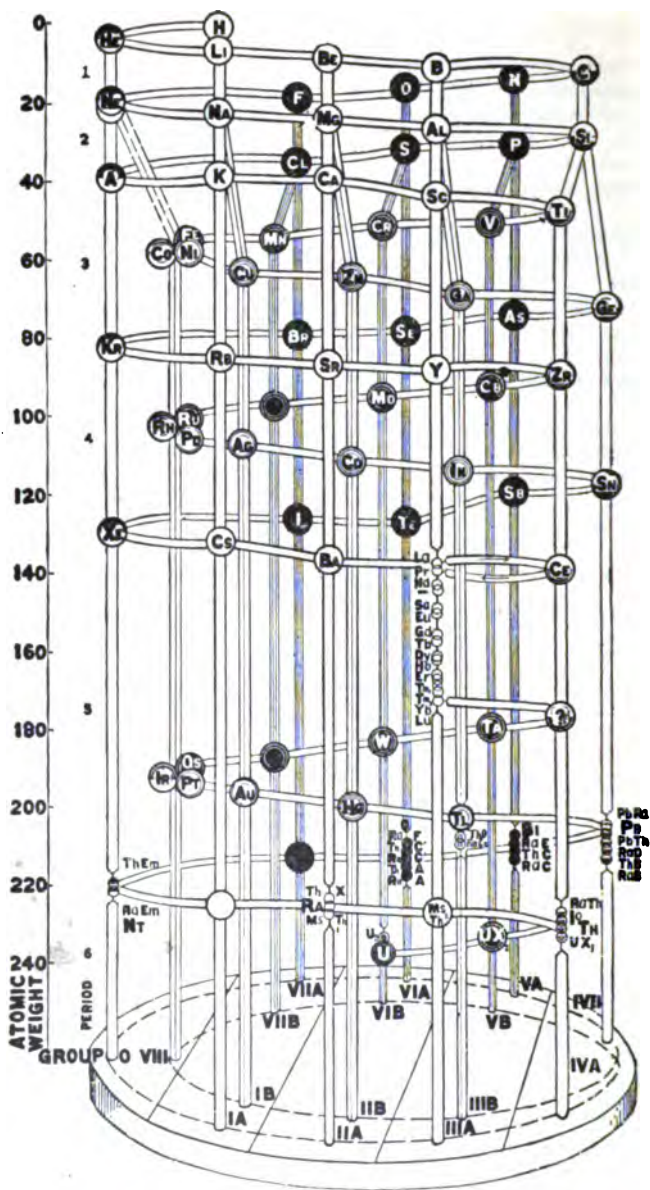
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PERIODIC TABLE OF HARKINS AND HALL

A periodic table of the elements arranged in the form of a helix

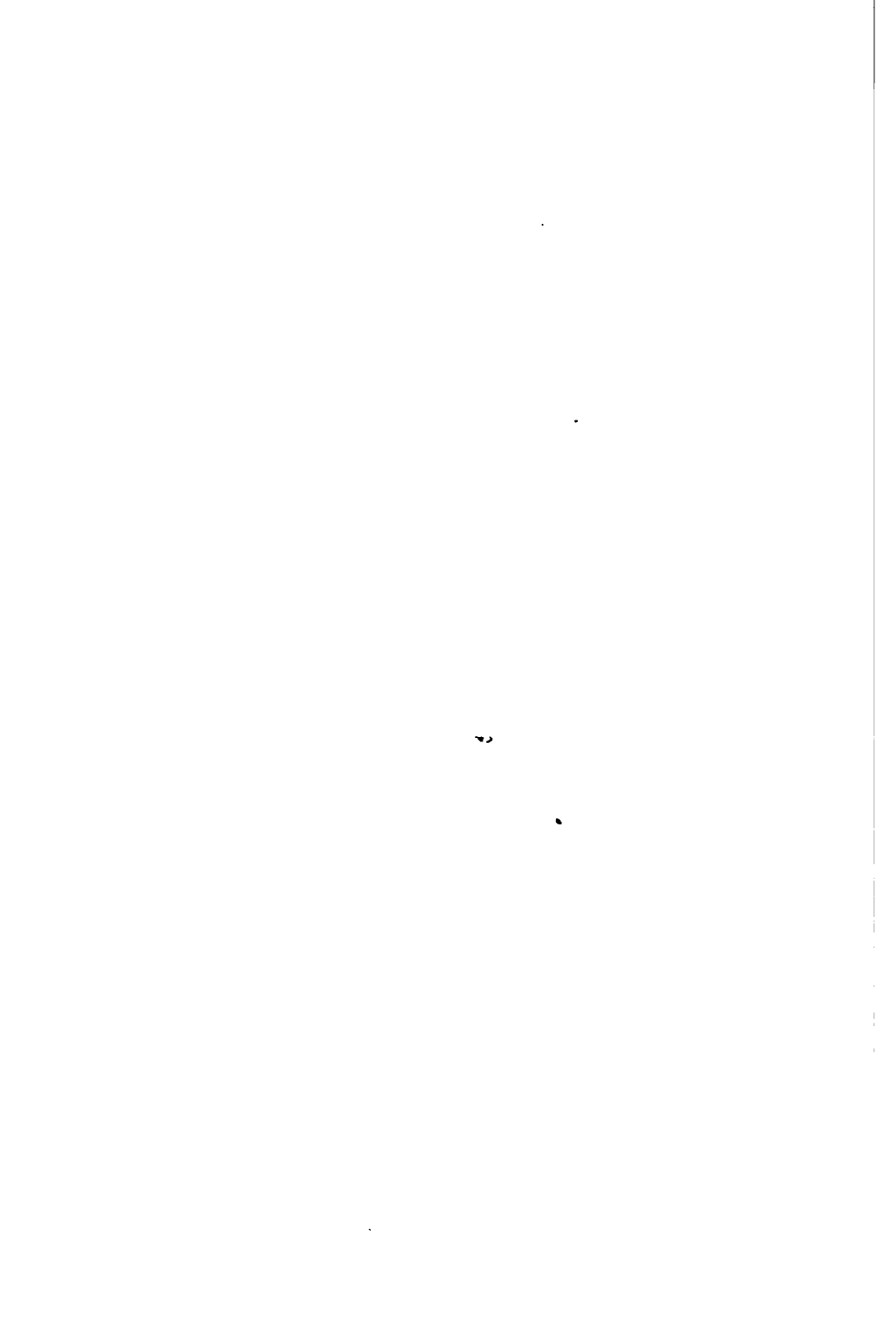
## APPENDIX A

### DENSITIES AND MELTING POINTS OF SOME OF THE ELEMENTS

	DENSITY	MELTING POINT		DENSITY	MELTING POINT
Aluminium . . .	2.65	658.7	Mercury . . . .	13.56	— 38.87
Antimony . . .	6.70	630.	Molybdenum . .	8.60	2550.
Arsenic . . . .	5.73	850.	Nickel . . . . .	8.90	1452.
Barium . . . . .	3.75	850.	Palladium . . .	12.44	1550.
Bismuth . . . .	9.80	271.	Phosphorus, yellow	1.83	44.
Boron . . . . .	2.5(?)	2200 to 2500	Platinum . . . .	21.50	1755.
Bromine . . . .	3.102	— 7.8	Potassium . . .	0.862	62.8
Cadmium . . . .	8.64	320.9	Radium . . . . .	(?)	700.
Calcium . . . .	1.55	810.	Selenium . . . .	4.80	220.
Carbon, Diamond	3.52		Silicon . . . . .	2.35	1420.
Carbon, Graphite	2.30	3600.	Silver . . . . .	10.50	960.5
Chromium . . . .	7.30	1615.	Sodium . . . . .	0.971	97.5
Cobalt . . . . .	8.60	1480.	Strontium . . . .	2.54	(?)
Copper . . . . .	8.93	1083.	Sulfur, monoclinic	1.96	119.2
Gallium . . . .	5.95	30.	Sulfur, rhombic .	2.06	112.8
Gold . . . . .	19.32	1063.	Tantalum . . . .	16.60	2900.
Iodine . . . . .	4.95	113.5	Tellurium . . . .	6.25	452.
Iridium . . . .	22.41	2350. (?)	Tin . . . . .	7.30	231.9
Iron . . . . .	7.86	1530.	Titanium . . . .	3.54	1800.
Lead . . . . .	11.37	327.4	Tungsten . . . .	18.72	3400.
Lithium . . . .	0.534	186.	Vanadium . . . .	6.02	1720.
Magnesium . . .	1.74	651.	Zinc . . . . .	7.10	419.4
Manganese . . .	8.01	1230.			

### HEAT OF COMBUSTION IN CALORIES PER GRAM-MOLECULAR VALUE BASED ON LANDOLT AND BÖRNSTEIN'S TABLES, FOURTH EDITION (Values at constant pressure)

COMPOUND	PRODUCTS OF COMBUSTION	HEAT OF COMBUSTION
Aluminium ( $\text{Al}_3$ ) . . . . .	$\text{Al}_2\text{O}_3$	386200.
Carbon (C) solid . . . . .	$\text{CO}$	29000
Carbon (C) solid . . . . .	$\text{CO}_2$	97000
Carbon monoxide ( $\text{CO}$ ) . . . . .	$\text{CO}_2$	68000
Hydrogen ( $\text{H}_2$ ) . . . . .	$\text{H}_2\text{O}$ (vapor)	58380
Hydrogen ( $\text{H}_2$ ) . . . . .	$\text{H}_2\text{O}$ (liquid)	69000
Sulfur (S) . . . . .	$\text{SO}_2$ (gas)	71080
Methane ( $\text{CH}_4$ ) . . . . .	$\text{CO}_2 + 2 \text{H}_2\text{O}$ (vapor)	192160
Methane ( $\text{CH}_4$ ) . . . . .	$\text{CO}_2 + 2 \text{H}_2\text{O}$ (liquid)	213500
Ethane ( $\text{C}_2\text{H}_6$ ) . . . . .	$2 \text{CO}_2 + 3 \text{H}_2\text{O}$ (vapor)	340300
Ethane ( $\text{C}_2\text{H}_6$ ) . . . . .	$2 \text{CO}_2 + 3 \text{H}_2\text{O}$ (liquid)	372300
Acetylene ( $\text{C}_2\text{H}_2$ ) . . . . .	$2 \text{CO}_2 + \text{H}_2\text{O}$ (vapor)	301680
Acetylene ( $\text{C}_2\text{H}_2$ ) . . . . .	$2 \text{CO}_2 + \text{H}_2\text{O}$ (liquid)	312300
Benzene ( $\text{C}_6\text{H}_6$ ) (liquid) . . . . .	$6 \text{CO}_2 + 3 \text{H}_2\text{O}$ (vapor)	749200
Benzene ( $\text{C}_6\text{H}_6$ ) (liquid) . . . . .	$6 \text{CO}_2 + 3 \text{H}_2\text{O}$ (liquid)	781200
Ethyl alcohol ( $\text{C}_2\text{H}_5\text{OH}$ ) (liquid) . . . . .	$2 \text{CO}_2 + 3 \text{H}_2\text{O}$ (vapor)	294700
Ethyl alcohol ( $\text{C}_2\text{H}_5\text{OH}$ ) (liquid) . . . . .	$2 \text{CO}_2 + 3 \text{H}_2\text{O}$ (liquid)	320700
Methyl alcohol ( $\text{CH}_3\text{OH}$ ) (liquid) . . . . .	$\text{CO}_2 + 2 \text{H}_2\text{O}$ (vapor)	149380





# APPENDIX B

## TABLE OF THE ELEMENTS

ELEMENT	SYMBOL	ATOMIC WEIGHT	ELEMENT	SYMBOL	ATOMIC WEIGHT
Aluminium . . .	Al	27.10	Molybdenum . .	Mo	96.00
Antimony . . .	Sb	120.20	Neodymium . .	Nd	144.30
Argon . . . . .	A	39.90	Neon . . . . .	Ne	20.20
Arsenic . . . .	As	74.96	Nickel . . . . .	Ni	58.68
Barium . . . .	Ba	137.37	Nitron . . . . .	Nt	222.40
Bismuth . . . .	Bi	208.00	Nitrogen . . . .	N	14.006
Boron . . . . .	B	10.90	Osmium . . . . .	Os	190.90
Bromine . . . .	Br	79.92	Oxygen . . . . .	O	16.00
Cadmium . . . .	Cd	112.40	Palladium . . . .	Pd	106.70
Cæsium . . . .	Cs	132.81	Phosphorus . . .	P	31.04
Calcium . . . .	Ca	40.07	Platinum . . . .	Pt	196.90
Carbon . . . . .	C	12.006	Potassium . . . .	K	39.10
Cerium . . . . .	Ce	140.26	Præseodymium .	Pr	140.90
Chlorine . . . .	Cl	35.46	Radium . . . . .	Ra	226.00
Chromium . . . .	Cr	52.00	Rhodium . . . . .	Rh	102.90
Cobalt . . . . .	Co	58.97	Rubidium . . . .	Rb	85.45
Columbium . . .	Cb	93.10	Ruthenium . . . .	Ru	101.70
Copper . . . . .	Cu	63.57	Samarium . . . . .	Sa	150.40
Dysprosium . . .	Dy	162.50	Scandium . . . .	Sc	44.10
Erbium . . . . .	Er	167.70	Selenium . . . . .	Se	79.20
Europium . . . .	Eu	152.00	Silicon . . . . .	Si	28.30
Fluorine . . . .	F	19.00	Silver . . . . .	Ag	107.88
Gadolinium . . .	Gd	157.80	Sodium . . . . .	Na	23.00
Gallium . . . . .	Ga	70.10	Strontium . . . .	Sr	87.63
Germanium . . .	Ge	72.60	Sulfur . . . . .	S	32.06
Glucinum . . . .	Gl	9.10	Tantalum . . . .	Ta	181.50
Gold . . . . .	Au	197.20	Tellurium . . . .	Te	127.60
Helium . . . . .	He	4.00	Terbium . . . . .	Tb	159.20
Holmium . . . .	Ho	163.50	Thallium . . . .	Tl	204.00
Hydrogen . . . .	H	1.008	Thorium . . . . .	Th	232.15
Indium . . . . .	In	114.80	Thulium . . . . .	Tm	168.60
Iodine . . . . .	I	126.92	Tin . . . . .	Sn	118.70
Iridium . . . . .	Ir	193.10	Titanium . . . .	Ti	48.10
Iron . . . . .	Fe	55.84	Tungsten . . . .	W	184.00
Krypton . . . . .	Kr	82.92	Uranium . . . . .	U	238.20
Lanthanum . . . .	La	139.00	Vanadium . . . .	V	51.00
Lead . . . . .	Pb	207.20	Xenon . . . . .	Xe	130.20
Lithium . . . . .	Li	6.94	Ytterbium	Yb	173.60
Lutecium . . . .	Lu	175.00	(Neoytterbium)		
Magnesium . . .	Mg	24.32	Yttrium . . . . .	Yt	89.30
Manganese . . . .	Mn	54.93	Zinc . . . . .	Zn	65.37
Mercury . . . .	Hg	200.60	Zirconium . . . .	Zr	90.60

# TENSION OF AQUEOUS VAPOR EXPRESSED IN MILLIMETERS OF MERCURY

(Physical and Chemical Constants, Kaye and Laby)

TEMPERATURE	PRESSURE	TEMPERATURE	PRESSURE	TEMPERATURE	PRESSURE
10°	9.20	21°	18.62	32°	35.53
11°	9.84	22°	19.79	33°	37.59
12°	10.51	23°	21.02	34°	39.75
13°	11.23	24°	22.32	35°	42.02
14°	11.98	25°	23.69	36°	44.40
15°	12.78	26°	25.13	37°	46.90
16°	13.62	27°	26.65	38°	49.51
17°	14.52	28°	28.25	40°	55.13
18°	15.46	29°	29.94	50°	92.80
19°	16.56	30°	31.74	100°	760.00
20°	17.51	31°	33.57		

## WEIGHT IN GRAMS OF 1 LITER OF VARIOUS GASES UNDER STANDARD CONDITIONS, AND BOILING POINTS UNDER PRESSURE OF 760 MILLIMETERS

NAME	WEIGHT OF 1 LITER	BOILING POINT	NAME	WEIGHT OF 1 LITER	BOILING POINT
Acetylene . . .	1.1621	- 88.8°	Hydrogen chloride	1.6398	- 83.1°
Air . . . . .	1.2928		Hydrogen fluoride	0.893	+ 19.4°
Ammonia . . . .	0.7708	- 33.5°	Hydrogen sulfide	1.5392	- 61.6°
Argon . . . . .	1.7809	- 186.0°	Methane . . . .	0.7168	- 164.0°
Carbon dioxide .	1.9768	- 78.2°	Nitric oxide . .	1.3402	- 153.0°
Carbon monoxide	1.2504	- 190.0°	Nitrogen . . . .	1.2507	- 195.7°
Chlorine . . . .	3.1674	- 33.6°	Nitrous oxide . .	1.0777	- 89.8°
Helium . . . . .	0.1782	- 268.7°	Oxygen . . . . .	1.4290	- 183.0°
Hydrogen . . . .	0.08987	- 252.7°	Sulfur dioxide . .	2.9266	- 8.0°

## ELECTROCHEMICAL SERIES

1. Cæsium	8. Aluminium	15. Nickel	22. Antimony
2. Rubidium	9. Manganese	16. Tin	23. Mercury
3. Potassium	10. Zinc	17. Lead	24. Silver
4. Sodium	11. Chromium	18. Hydrogen	25. Palladium
5. Lithium	12. Cadmium	19. Copper	26. Platinum
6. Calcium	13. Iron	20. Arsenic	27. Gold
7. Magnesium	14. Cobalt	21. Bismuth	28. Osmium

## RELATION BETWEEN ENGLISH AND METRIC CONSTANTS

1 lb. (troy) = 373.24 grams	1 l. = 1.05668 United States quarts
1 oz. (troy) = 31.10848 grams	1 gal. = 3.78543 liters
1 lb. (avoirdupois) = 453.59 grams	1 cc. = 0.0610 cubic inch
1 oz. (avoirdupois) = 28.3496 grams	1 cu. in. = 16.3872 cubic centimeters
1 kg. = 2.67928 lb. (troy)	1 cu. ft. = 28,320 cubic centimeters
1 kg. = 2.20462 lb. (avoirdupois)	1 cm. = 0.3937 inch
	1 m. = 39.37 inches

